PB82-231945

Control of Sulfur Emissions from Oil Shale Retorts

IT Enviroscience
Knoxville, TN

Prepared for

Industrial Environmental Research Lab.
Cincinnati, OH

Apr 82

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-82-016
2. ORD Report
3. RECIPIENT'S ACCESSION NO. PB82-231945
4. TITLE AND SUBTITLE
Control of Sulfur Emissions from
Oil Shale Retorts
5. REPORT DATE April 1982
6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) R. J. Lovell, S. W. Dylewski, C. A. Peterson
8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS
IT Enviroscience
Knoxville, TN 37923
10. PROGRAM ELEMENT NO. CCZNIA
11. CONTRACT/GRANT NO. Contract No. 68-03-2568
T-7012
12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Protection Agency
Office of Research and Development
Industrial Environmental Research Laboratory
Cincinnati, OH 45268
13. TYPE OF REPORT AND PERIOD COVERED Final 7/79 - 7/80
14. SPONSORING AGENCY CODE EPA 600/12
15. SUPPLEMENTARY NOTES
16. ABSTRACT

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The work conducted included an in-depth evaluation of available gas characterization data from all major oil shale development operations in the United States. Data gaps and inconsistencies were identified and corrected where possible through working with the developers and/or researchers in the field. From the gas characterization data, duty requirements were defined for the sulfur removal systems. Based on this information, Stretford gas sweeting technology was recommended, and the design of a 1000 CFM pilot plant was completed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Oil Shale Emissions Control Technology Pilot Plant Design	Hydrogen sulfide control Control technology costs	

18. DISTRIBUTION STATEMENT Unrestricted	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 192
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

EPA 600/7-82-016
April 1982

PB82-231945

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Contract 68-03-2568

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CINCINNATI, OHIO 45268

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U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs.

Synthetic fuel processes under development must be characterized prior to commercialization so that pollution control needs can be identified and control methods can be integrated with process designs. Shale oil recovery processes are expected to have unique air, water, and solid waste pollution control requirements. This report describes an in-depth evaluation of the control technology systems that are applicable to the removal of hydrogen sulfide from retort off-gases. Further information on the environmental aspects of oil shale processing and control technology can be obtained from IERL-Ci, Oil Shale and Energy Mining Branch.

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Director
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ABSTRACT

The objectives of this study were to determine the most applicable control technology for control of sulfur emissions from oil shale processing facilities and then to develop a design for a mobile slipstream pilot plant that could be used to test and demonstrate that technology.

The work conducted included an in-depth evaluation of available gas characterization data from all major oil shale development operations in the United States. Data gaps and inconsistencies were identified and corrected where possible through working with the developers and/or researchers in the field. From the gas characterization data, duty requirements were defined for the sulfur removal systems. Based on this information, Stretford gas sweeting technology was recommended, and the design of a 1000 CFM pilot plant was completed.

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I. PROJECT SUMMARY

A. INTRODUCTION

The future beneficial use of the nation's extensive oil-shale resources depends not only on the development of suitable process economics but also on the development of suitable environmental controls. Even though the oil that would be produced is comparatively low in sulfur content, the potential sulfur emissions from large-scale production of shale oil could be enormous. Oil shale contains up to about 2% sulfur. A typical shale in the Green River Formation in Colorado contains about 0.7% sulfur. When the shale is retorted, somewhere between 16 and 30% of the sulfur is liberated to the gas stream, with the majority remaining with the spent shale. The emissions from a 64,000-m^3/day oil-shale industry could be as high as 691-1273 tonnes per day if emission controls were not applied. If conventional flue-gas scrubbing systems were used to control the emissions for which the average reduction achieved is 90%, the controlled emissions would be 69 to 127 tonnes day. However, if the sulfur could be removed before the gas is burned, in which case the average reduction is 98%, the controlled emissions would be in the order of 14 - 26 tonnes/day.

Gases produced by direct-fired retorts, either above ground or in-situ, are significantly different from gases normally encountered in application of desulfurization technology that the technology cannot just be transferred. Gases from direct-fired retorts contain large amounts of inert components and have a high ratio of carbon dioxide (CO_2) to hydrogen sulfide (H_2S); they also contain large amounts of ammonia and unsaturated hydrocarbons, such as acetylene, ethylene, propylene, butylene, and butadiene. The gases are saturated with water and contain some oxygen and trace amounts of sulfur species other than H_2S.

The large amounts of CO_2 in the gases and the high CO_2/H_2S ratios make it impractical to employ many of the desulfurization technologies. Since the gases are produced in huge volumes at near-atmospheric pressures, many other desulfurization processes cannot be economically applied. Those processes that can be applied may be only marginal in performance because of the large amounts of CO_2 and the presence of oxygen and/or unsaturated hydrocarbons in the gases or because the gas may contain a large amount of organic sulfur.

Oil-shale developers are involved in a number of significant pilot-scale activities for the development of retorting process technology, and have indicated to the United States Environmental Protection Agency (EPA) their willingness to cooperate on joint projects for sulfur control technology evaluation. To capitalize on this opportunity and to explore the possibility that sulfur emission control will be more of a problem than was orginally thought, EPA contracted with IT Enviroscience, Inc., to investigate the various commercial sulfur-removal technologies and to propose a pilot-plant design based on the most cost-effective process for the removal of gaseous sulfur compounds from oil-shale retort gases.

B. OBJECTIVES

The objectives of this study were to determine the most applicable control technology for control of sulfur emissions from oil shale processing facilities and then to develop a design for a mobile slip-stream pilot plant that could be used to test and demonstrate that technology.

C. APPROACH

The work conducted included an in-depth evaluation of available gas characterization data from all major oil-shale development operations in the United States. Data gaps and inconsistencies were identified and corrected where possible through working with the developers and/or researchers in the field. From the gas characterization data, duty requirements were defined for the sulfur removal systems. It was found that oil-shale retorting processes fall into two broad categories: direct-fired-retort processes and indirect-heated-retort processes, each category having distinctly different duty requirements.

The overriding factor that separates the two categories of retorting processes and that is dominant in the application of desulfurization technology is the CO_2/H_2S ratio of the gas produced from the retort. Those from direct-fired retorts have CO_2/H_2S ratios that range from 76 to more than 165 and thus would require that the sulfur-removal process selectively remove H_2S in the presence of large amounts of CO_2. Indirect-heated retorts produce gases with CO_2/H_2S ratios in the range of 4.3 to 5, which would allow a nonselective process to be used.

During this study it was determined by the EPA that the greatest immediate concern is control of sulfur emissions from direct-fired oil-shale retorting processes and that the pilot-plant design should be applicable to these retorting methods. Since application of desulfurization technology to gases from direct-fired-retorting processes is more limiting, the screening of available process technologies was based on the duty requirements for those gases.

D. RECOMMENDED AVAILABLE H_2S CONTROL TECHNOLOGY

The class of processes that remove H_2S and CO_2 from fuel gases is generically called acid-gas removal or gas-sweeting processes. Removal of acid gases and/or other gaseous impurities from gas streams is accomplished either by direct chemical conversion of the acid gas to another compound that can be more easily separated from the gas, by absorption into liquid, or by adsorption on a solid. The large volumes of gas that must be processed in a typical oil-shale plant will limit the application of desulfurization technology to high-capacity, liquid-phase processes. Since CO_2 is absorbed to some extent by all liquid-phase processes, the high CO_2/H_2S ratio of the gas limits the selection to those processes that can selectively absorb sulfur compounds in the presence of large amounts of CO_2.

Of those processes that selectively remove H_2S by direct conversion of the H_2S to elemental sulfur, the Stretford process is the most effective one. Of those indirect processes that selectively remove H_2S by separating the H_2S as a concentrated acid-gas stream, the following processes were selected as the most effective in their separate process classifications: the Selectamine and the Adip processes, which use MDEA as the absorbent, the Benfield, the Selexol, and the Diamox processes. The Benfield and Selexol processes require the gas to be at high pressure and thus were eliminated since compression of the gas for the purpose of desulfurization could not be economically justified.

Except for the Diamox process, all the candidate processes are capable of removing H_2S down to about 10 ppmv. However, organic sulfur compounds, principally COS, which exist in only trace amounts in the gas, are not significantly removed or are only partly removed by the various processes. However, the presence of those compounds may reduce the overall effectiveness to 98%.

For desulfurization of gases from direct-fired oil-shale retorts the Stretford direct process is the most cost-effective system. For the model case used to evaluate the various processes the total estimated cost of sulfur removed by the Stretford process would be about $0.50 per barrel of oil produced, which is less than half that projected for the best of the other processes evaluated.

The Claus process is used to recover sulfur from the acid gas produced by the indirect sulfur-removal processes. The large amount of CO_2 in the gas makes the best of the indirect processes only marginally capable of producing an acid gas rich enough in H_2S for processing by the Claus process. Thus to apply these processes multiple stages of selective absorption would be required to handle the gas produced by many of the direct-fired retorts. The process, however, does not effectively remove COS. Only trace quantities of COS (less than 50 ppmv) have been found in gases produced by direct-fired retorts and thus an overall effectiveness of 98% or more is projected for the Stretford process. If the quantity of COS in the gas should be higher than indicated by the currently available gas characterication data the removal efficiency could be less than 98%.

The Stretford direct process, on the other hand, is only minimally affected by the quantity of CO_2 in the gas and therefore is adaptable to the full range of gases produced by direct-fired retorts.

E. DESIGN OF PILOT PLANT

The pilot-plant design is based on the current state-of-the-art technology for commercial application of the Stretford process. The maximum design capacity of the unit is 28.3 sm^3m of feed gas and 6.6 Kg of sulfur per hour. The plant should be capable of reducing the H_2S content of the gas to 10 ppmv or less, and CO_2/H_2S ratios as high as 200 to 1 should be possible.

The pilot plant is sized primarily to remove H_2S from oil-shale gas produced by direct-fired retorts. However, use of an ejector-venturi gas-scrubbing system affords wide gas turndown capability for the system. The pilot plant thereby is capable of operating on a slip stream from any of the currently proposed direct or indirect oil-shale retorting processes in the United States.

To properly function, the feed gas to the pilot plant must be 120°F or less, with most of the ammonia removed. A gas cooling column has been incorporated into the pilot design for cooling and removing the ammonia from the feed gas. The estimated cost of the pilot plant with all equipment, instruments, and controls, assembled on skid mountings as a complete and operable unit, is as follows:

Range	With Cooler	Without Cooler
High	$520,000	$338,000
Probable	400,000	260,000
Low	308,000	200,000

F. CONCLUSIONS

The Stretford direct gas desulfurization process may be the only currently available commerical process capable of effectively removing H_2S from gases produced by direct-fired retorts. Application of the Stretford process or of any other process to the treatment of these gases would extend the technology of the process into areas in which no analogous experience is available. Many questions need to be answered before the process can be applied with confidence to a full-scale commercial shale-oil production facility.

The principal areas of concern are as follows:

1. absorption of CO_2 versus gas characteristics,
2. capacity of the solution for absorbing sulfur versus gas characteristics,
3. rate of by-product thiosulfate formation versus gas characteristics,
4. disposition of COS and other organic sulfur compounds in the feed gas,
5. effects of unsaturated hydrocarbons in the feed gas on process operation, life of the Stretford chemicals, and quality of the sulfur produced.

The viability of the oil-shale industry hinges on an environmentally compatible sulfur-removal process. Although there are no federal industry standards for emissions for the oil-shale industry at this time, the State of Colorado has enacted legislation that limits industry emissions to less than 0.3 lb of sulfur dioxide per barrel of oil produced and an equal amount per barrel of oil refined. To meet this standard at least 96% of the sulfur in the gas expressed as SO_2 would have to be removed.

The area of air pollution compliance that is of the greatest concern to industry and government is the Prevention of Significant Deterioration (PSD) requirements of the Federal Clean Air Act. This concept was enacted to prevent the addition of specified pollutants above a prescribed baseline value in specified air regions. Colorado adopted a more stringent plan, which limits the maximum level of sulfur dioxide in the air to an annual average of 10 μg/m³. Thus the maximum quantity of shale oil that can be produced will be limited by the effectiveness of the sulfur emission control system used.

Unless the Stretford process can be demonstrated as an effective and reliable process for treatment of direct-fired oil-shale gases, industry may have to resort to combusting the gas first and then using less effective flue-gas disulfurization techniques. Because of the stringent PSD requirements any increase in sulfur emissions could result in reduction of the potential production capacity of the shale-oil industry.

II. INTRODUCTION

A. OIL-SHALE RESOURCE[1]

Recently, as the price of imported oil began to rise and gasoline exceeded $1.00/gal, interest was renewed in obtaining oil from oil shale as part of the solution to the energy problem. The solutions to the environmental problems that were once a cost deterrent to commercialization have become more acceptable now that crude-oil prices are exceeding $20.00 per barrel.

The consumption of oil in the United States in 1978 was about 6 billion barrels. It has been estimated that the known oil-shale resources that could be tapped by use of existing technology are equivalent to 600 billion barrels, and the total resources in the Green River Formation in the west have been estimated at 2 trillion barrels of oil, which would provide oil for 100 and 333 years, respectively, based on the 1978 rate of consumption. There are very sizable deposits of shale in the east and midwest, which are referred to as Devonian shale. These shales are leaner in oil than western (Eocene) shales; but, if they are incorporated into the resource estimate, the total amount climbs to about 28 trillion barrels. With a resource of this magnitude available, some people would ask why we import almost half of our oil supply. Part of the answer lies in the fact that the organic fraction of the shale is small and that, if the yield is assumed to be 24 gal/ton of shale, about 1 cubic mile of rock would have to be processed to yield the oil we consumed in 1978. Another part of the answer is that sizable quantities of environmentally undesirable components could be released to the air and to surface waters.

B. ENVIRONMENTAL CONSTRAINTS[1]

Sulfur, one of the undesirable components, is contained in oil shale up to about 2%, and a typical shale in the Green River Formation may contain 0.7%.[2] Partitioning studies[2,3] indicate that somewhere between 16 and 30% is liberated to the gas that is generated, with the majority of the sulfur remaining with the spent shale. Under some circumstances oil produced from shale might be considered to be a low-sulfur resource; in this case, however, where immense volumes of rock are processed, the potential for sulfur emissions is sizable. The uncontrolled sulfur emissions from an 8,000 m^3/day oil shale retort installation could be 86--.59 tonnes per day. The resulting impact on the semiarid region in the west would be significant.

The National Ambient Air Quality Standard (NAAQS) for sulfur dioxide limits the annual average to 80 $\mu g/m^3$ of air. If this were the only regulation that industry had to comply with, all sulfur species would probably be oxidized to sulfur dioxide and some form of flue gas desulfurization would be used for control. However, the oil-shale industry must also be concerned with regulations dealing with the amount of a specific material that may be emitted by a specific source. Although there are no federal industry standards for emissions for the oil-shale industry at this time, the State of Colorado has enacted legislation that limits industry emissions to less than 0.3 lb of sulfur dioxide per barrel of oil produced and an equal amount per barrel for oil refined. The area of air pollution compliance that is of the greatest concern to industry and government is the Prevention of Significant Deterioration (PSD) requirements of the Federal Clean Air Act. This concept was enacted to prevent the addition of specified pollutants above a prescribed baseline value in specified air regions. Colorado adopted a similar plan, but made the acceptable levels for PSD more stringent. Table II-1 summarizes the PSD requirements for the federal government and the State of Colorado, which puts limits on sulfur dioxide to an annual average of 10 $\mu g/m^3$. The future potential of the oil-shale industry therefore hinges on the effectiveness of the sulfur-removal process.

C. PURPOSE OF STUDY

Oil-shale developers are involved in a number of significant pilot-scale activities for the development of process technology, and have indicated to the EPA their willingness to cooperate on joint projects for sulfur control technology evaluation. To capitalize on this oppor-

Table 1. Maximum Concentration of SO_2 to Meet Colorado and Federal PSD Requirements

	SO_2 Maximum Concentration ($\mu g/m^3$)	
	Colorado	Federal
Class I[a]		
Annual average	2	2
24-hr maximum	5	8
3-hr maximum	25	25
Class II[b]		
Annual average	10	20
24-hr maximum	50	91
3-hr maximum	300	512

[a] Class-I areas are listed as national parks and as natural wilderness and primitive areas.

[b] Class-II areas are the rest of the country.

tunity and to explore the possibility that sulfur emission control will be more of a problem than was originally thought, EPA contracted with IT Enviroscience, Inc., to propose a pilot-plant design based on the most cost-effective process for the removal of gaseous sulfur compounds, as well as one that is mobile. This type of design would necessitate investigation of various commercial sulfur-removal technologies and their applicability to oil-shale gases.

D. APPROACHES AND LIMITATIONS

1. Alternatives for Control of Sulfur Emissions

Two approaches can be taken to control sulfur emissions: to remove sulfur compounds from the gas before it is combusted (a gas-sweetening process), thereby producing a sulfur-free fuel; or to first combust the gas and then remove the resulting SO_2 from the flue gases [flue-gas-desulfurization (FGD) process].

The latter approach is generally less effective, because most of the flue-gas scrubbers can remove only 90 to 95% of the sulfur in the flue gas. The volume of gases handled by the FGD process is much larger than that handled by the first process because the products of combustion are more voluminous than the fuel gas burned. Also, the FGD system generally consumes more water and chemicals and is more costly to operate than the gas-sweetening processes.[4]

Processes that remove sulfur from the fuel gas before it is combusted are generally more effective, with most processes capable of removing 98% or more of the H_2S in the gas. With these processes, however, sulfur in other forms, such as COS, CS_2, and mercaptans, may be only partly removed or not removed at all.

To meet the Colorado air quality control regulations of 0.3 lb/bbl of SO_2 equalivant emissions, at least 95% of the sulfur in the gas would have to be removed. For these reasons this study was directed toward the more effective fuel-gas desulfurization techniques.

2. Basis of Process Selection

During this study it was determined by the EPA that the greatest immediate concern was control of sulfur emissions from direct-fired oil-shale retorting processes and that the pilot-plant design should be applicable to these retorting methods. Therefore the screening of available process technologies was based on the duty requirements for desulfurization of direct-fired retort gases.

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph of captioned material, the earlier reference number may not apply to that particular portion.

III. OIL-SHALE GAS CHARACTERIZATION

A. CHARACTERIZATION OF OIL SHALES

1. Introduction

In characterizing the gas produced by the various oil-shale retort processes, it is necessary to have some understanding of the nature and composition of the organic and mineral materials that comprise oil shale and of how the materials become distributed among the resulting products. The oil in oil shale can be neither squeezed nor drained out at ambient or moderately elevated temperatures. When the oil shale is heated to temperatures in excess of 200°C and up to 500°C, the material is destructively distilled, producing recoverable oil and gas and leaving a spent mineral residue.

2. Composition of Oil Shale

Oil shales having similar assays of oil, in gallons per ton (gpt), were found also to have a fairly narrow range of compositions, as can be seen in Table 2.[1,2] However, even in the Mahogany ledge, which is about 21 m thick, the assay of oil varies from 37.5 to 312.3 ℓp tonne.

The mineral material, after being fired to an ash, has the composition shown in Table 3.[1] The minerals in their natural form in oil shale are varied and complex, and on a point-to-point basis the pH can vary from 8.5 to 10.[3]

3. Composition and Nature of Organic Matter in Oil Shale

The organic matter in Green River oil shale has a significant amount of hydrogen (see Table 4).[1,4] The ratio of about 1.5 moles of hydrogen per mole of carbon enabled about two-thirds of the organic matter to be converted to oil during retorting. In contrast, high-volatility bituminous coal has a hydrogen-to-carbon mole ratio of about 0.9 to 1.[3]

The substantial amount of oxygen present in the organic material indicates the likely presence of carboxyl groups. It is also likely that

Table 2. Properties of Green River Mahogany Ledge Oil Shale

Component	Amount (wt % of raw shale) Stanfield[a]	 Smith[b]
Carbon, organic	12.4	12.21
Hydrogen	1.8	1.76
Nitrogen	0.4	0.37
Sulfur	0.6	0.70
CO_2, mineral	18.9	17.92
Ash	65.7	
Mineral content of spent shale	———	65.26
	99.8	98.22

[a] See ref 1; analysis based on sample that yielded 115 ℓ/tonne.

[b] See ref 2; analysis based on sample that yielded 105 ℓ/tonne.

Table 3. Ash Composition of Oil Shale[a]

Component	Amount (wt % of raw shale)
SiO_2	27.8
Fe_2O_3	3.0
Al_2O_3	8.6
C_aO	15.1
M_gO	6.5
SO_3	1.2
Na_2O	2.0
K_2O	1.5

[a] Oil assay, 115 ℓ/tonne (see ref 1).

Table 4. Composition of Organic Matter in Green River Oil Shale

Component	Amount (wt % of raw shale)	
	Stanfield[a]	Smith[b]
Carbon	76.5	80.5
Hydrogen	10.5	10.3
Nitrogen	2.5	2.4
Sulfur	1.2	1.0
Oxygen	9.3	5.8

[a] See ref 1; analysis based on sample that yielded 115 ℓ/tonne

[b] See ref 2; analysis based on sample that yielded 105 ℓ/tonne

these carboxyl groups are saponified by the mineral material, whose pH after pyrolysis is about 11.[5] Therefore only through pyrolysis, or destructive distillation, wherein organogenic CO_2 is released, can oil be recovered from oil shale. As further evidence of the change in the nature of the organic material, as implied by the term "destructive distillation," the oil produced from oil shale has a pour point of about 29°C, although oil will not drain from oil shale at this temperature.

The presence of sulfur and nitrogen in oil shale and shale oil is discussed below.

4. Recovery of Products from Pyrolysis of Oil Shale by the Modified Fischer Method

A quantity of oil shale representing 94 ℓpt assay was obtained from 10 locations in the Green River formation and was blended to provide a quantity of uniform composition. Eight replicate pyrolysis runs were made by the modified Fischer method to determine the reproducibility of this method of assaying the yield of oil and gas from oil shale.[2] Table 5 gives the quantity and composition of the gas produced during pyrolysis; the data, in material balance form, that were obtained are given in Table 6.

The recovery of materials expressed as percent of element contained in raw shale is shown in Table 7. These data show that the recovery of nitrogen in the oil and gas streams combined is only 53%, of which 8.6% is in the gas stream. They also show that the combined recovery of sulfur is only 25%, of which 16.9% is in the gas stream, and that if the shale oil were treated to remove nitrogen and sulfur the NH_3 content of the gas would increase about sixfold and the H_2S content would increase by 50%.

5. Sulfur Chemistry Relating to Pyrolysis Gas

The oil shale in the Green River formations contains sulfur in two major forms: organic (with -C-S- groups present) and pyrite, FeS_2.

Table 5. Gas Produced by Pyrolysis of Oil Shale by Modified Fischer Method

	Amount of Gas Produced	
Component	(vol %) (DG)[a]	(sm^3/tonne of raw shale)[b]
CH_4	17.44	4.7
C_2	5.44	1.5
$C_2^{=}$	2.10	0.6
C_3	2.43	0.6
$C_3^{=}$	2.39	0.6
C_4	1.50	0.4
$C_4^{=}$	0.60	0.2
C_4	1.20	0.03
$C_5^{\equiv}$	1.56	0.3
$C_5^{=}$	1.45	0.4
$C_6^{=}$	0.11	0.4
CO_2	24.00	6.5
CO	5.09	1.4
H_2	29.36	7.9
H_2S	3.20	0.9
NH_3	2.12	0.6
Total	100.00	27.03

[a] See ref 2.

[b] Calculated gas production.

Table 6. Material Balance on Pyrolysis of Oil Shale by Modified Fischer Method[a]

Component	Amount in Raw Shale (kg/tonne)	Retorted Product (kg/tonne of raw shale) Spent Shale	Oil	Gas	Water
Carbon, organic	121.9	28.7	80.3	14.3[b]	
Hydrogen, organic	17.7	2.0	11.0	3.1	1.5
Nitrogen	3.8	1.8	1.7	0.3	
Sulfur	6.8	5.1	0.5	1.2	
Minerals[c]	849.8	825.4	1.5	9.1	12.5
Totals	1000.0	863.0	95.0	28.0	14.0
	100%	86.3%	9.5%	2.8%	1.4%

[a] See ref 2.

[b] Including 1.6 kg of carbon from mineral carbon.

[c] Including mineral CO_2 and H_2O.

[d] Determined by oxygen balance.

[e] Including oxygen as CO and CO_2.

Table 7. Distribution of Elements in Products of Pyrolysis of Oil Shale[a]

	Distribution (wt %)			
Component	Spent Shale	Oil	Gas	Water
Carbon, organic	23.6	65.9	10.5	
Hydrogen, total	11.4	61.9	18.0	8.7
Nitrogen, total	46.6	44.8	8.6	
Sulfur, total	75.1	8.0	16.9	

[a] See ref 2.

The -C-S- groups are pyrolyzed in the presence of hydrogen to yield H_2S. Examination of the gas phase that is formed in this process indicated that it went to completion; but since there are still sulfur-containing organic compounds in the shale oil, the existence of small quantities of low-boiling organic sulfur compounds in the gas would not be surprising.

Pyrite can undergo hydrogenolysis to yield H_2S as shown below:

$$\underset{\text{(pyrite)}}{FeS_2} + \underset{\text{(hydrogen)}}{H_2} \longrightarrow \underset{\text{(iron sulfide)}}{FeS} + \underset{\text{(hydrogen sulfide)}}{H_2S}$$

Consequently one-half of the sulfur is available for recovery as H_2S and can appear in the gas. Sulfate salts, which are found in spent shales, are apparently formed in the combustion zone following pyrolysis.[6] Table 8 shows the estimated quantity of sulfur in these two forms and the sulfur available for recovery (3.89 kg/tonne of raw shale). The sulfur recovered as H_2S (1.15 kg/tonne of raw shale; see Table 6) is estimated to be 30% of the sulfur available for recovery.

B. PARAHO RETORT GAS

1. Introduction

Development Engineering, Inc. (DEI), a subsidiary of Paraho Development Corp., have developed an above-ground retort to the point that they are ready to design a commercial-size module. This retort can be designed to operate in either the direct mode, wherein combustion air is brought into direct contact with the shale in the retort, or in the indirect mode, wherein only recycled reheated pyrolysis gas is brought into contact with the shale. In the latter case the recycle gas is reheated by some of the pyrolysis gas being burned in a separate unit.[7] Recently, DEI concluded that the direct mode is more energy efficient, and they are now emphasizing its development in preference to the indirect mode.[8]

Table 8. Estimated Distribution of Sulfur in Oil Shale[a]

Sulfur Form	Distribution (kg/tonne of raw shale)	
	Total Sulfur	Available as H_2S
Organic	1.52[b]	1.52
Pyrite	4.73[c]	2.37
Unaccountable	0.75[d]	
Total	7.00	3.89

[a] Oil assay, 104 ℓ/tonne.

[b] Based on 0.45 kg of S/36.6 kg of C; see ref 4.

[c] Based on 1.41 kg of S as pyrite/ 45 kg of S as organic; see ref 4.

[d] Calculation based on 7.0 kg of total S per tonne of raw shale.

DEI has submitted a proposal in response to a Department of Energy (DOE) Program Opportunity Notice (PON) for the design, construction, and operation of an above-ground retort process as part of DOE's plan to develop technology to exploit oil shale as an energy resource. The PON requires that such a retort process produce shale oil at the rate of 960 m^3PD.[9]

2. Paraho Retort Process Description

In the direct mode of operation of the Paraho retort (see Fig. 1) crushed raw shale is fed to the top of the retort and spent shale leaves at the bottom. The shale passes downward by gravity successively through a mist formation and preheating zone, a retorting zone, a combustion zone, and finally, a residue-cooling, gas-preheating zone. The carbonaceous residue on the retorted shale is burned in the combustion zone to provide the principal fuel for the process.[10]

The shale-oil vapors produced in the retorting zone are cooled to a stable mist by the incoming raw shale, and leave the retort at approximately 60°C. This mist is sent to a roughing cyclone, a condenser, and finally a wet electrostat precipitator, for oil separation. A portion of the cooled, oil-free, retort gas that remains is recycled to the retort. The remainder of the product gas is sent to the desulfurization train.[10]

3. Basis of Retort Design and Operation

It is understood that the Paraho retort will be designed according to the parameters shown in Table 9. The process will be operated on a sustained basis in order to prove the process and to develop engineering data on all streams.[9,11]

4. Oil-Shale Composition

It is estimated that the oil shale to be used at the Paraho site will have the average composition discussed in Sect. III-A and summarized in Table 10.[4,9]

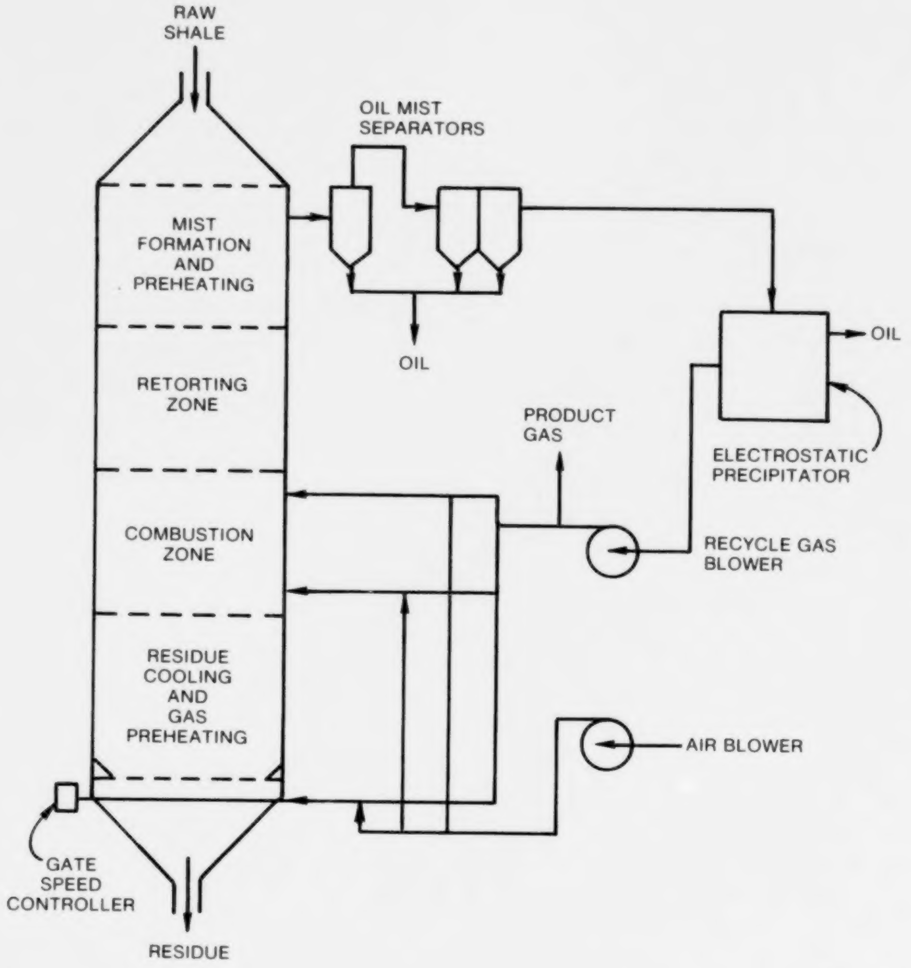

RAW SHALE
OIL MIST SEPARATORS
MIST FORMATION AND PREHEATING
OIL
OIL
RETORTING ZONE
PRODUCT GAS
ELECTROSTATIC PRECIPITATOR
COMBUSTION ZONE
RECYCLE GAS BLOWER
RESIDUE COOLING AND GAS PREHEATING
AIR BLOWER
GATE SPEED CONTROLLER
RESIDUE

Figure 1. Flow Diagram for Paraho Direct-Mode Retort

Table 9. Design Basis for Paraho Retort[a]

Shale-oil production	960 m^3/day
Oil-shale throughput	10,000 tonnes/day
Oil-shale assay	91.6—158 ℓ/tonne
Method of heating	Direct fired
Gas recycle ratio	498 sm^3/tonne
Gas production ratio	223 sm^3/tonne
Gas mole ratio, CO_2/H_2S	76
Heat content, HHV	105,400 joules
Pressure	Atmospheric
Temperature	60°C

[a] See refs 9 and 11.

Table 10. Estimated Composition of Green River Oil-Shale for Paraho PON Retort[a]

Component	Amount (wt %)
Carbon, organic	12.2
Carbon, mineral CO_2	4.9
Hydrogen	1.76
Nitrogen	0.37
Sulfur, organic	0.15
Sulfur, pyrite	0.47
Sulfur, sulfate	0.08
Oxygen, except CO_2	1.37
Balance, minerals	78.7
	100.0

[a] Oil assay, 104 to 112 ℓ/tonne (see refs 4 and 9).

5. Retort-Gas Characterization

As the pyrolysis gas is produced, 498 sm^3 of the gas per tonne of shale is recycled with sufficient air to provide the necessary heat for pyrolysis, and 223 sm^3/tonne is forwarded for uses external to the retort process. The gas produced is discharged at essentially atmospheric pressure and at about 60°C (see Table 11).

Although the gas from the Paraho retort has been sampled, analyzed, and reported over the years, only the most recent data are considered as adequately representative of the process because the techniques and methods used now are considered to be better than those used before 1977.[8] Table 11 shows the mean values of the composition of the gas produced by the Paraho retort in the direct mode during 1977 and 1978. In 1977, 31 gas samples were taken and analyzed and in 1978 there were 51. The high, low, and mean values for CO_2 H_2S, and NH_3 are shown in Table 12.[12]

C. OCCIDENTAL VERTICAL, MODIFIED, IN-SITU-RETORT GAS

1. Introduction

For more than six years Occidental Oil Shale, Inc. (OOSI) (formerly Garrett Research and Development Co.) has been engaged in modified, in-situ, process technology development. Occidental's philosophy in developing this process for producing oil from shale is to maximize the recovery of in-place oil while minimizing costs and the environmental impact.[13]

OOSI prepared and processed its fifth and sixth retorts under a cooperative program with the Department of Energy (formerly the Energy Research and Development Administration). The DOE/Occidental Cooperative Agreement is a two-phase agreement consisting of engineering development of two specific retort designs for the Occidental modified in-situ process as the first phase and a technical feasibility demonstration as the second phase.[13]

Table 11. Gas Produced by Paraho Direct-Fired Retort[a]

Component	Amount (sm^3/tonne)	Amount (dry vol %)
CH_4	4.8	2.16
C_2	1.2	0.56
C_2	1.5	0.66
C_3'S	1.6	0.71
C_4'S	1.2	0.56
C_5'S	1.2[b]	0.57[b]
CO_2	50.6	22.81
CO	5.5	2.50
H_2	10.5	4.74
H_2S	0.7	0.30
NH_3	1.6	0.70
N_2	141.5	63.80
O_2	0.2	0.09
SO_2		(17 ppm)
NO_x		(168 ppm)
CS_2, RSH, COS		None detected
Thiophene[a]		(50 ppm)
Thio-4-(methylthio)-3-cyclo-pentene-2-one[c]		(200 ppm)
Total, DG	222.2	100
H_2O		20[d]

[a] Oil assay, 100 to 108 ℓ/tonne; see ref 12.

[b] Total for C_5 and higher hydrocarbons.

[c] Identified sulfur compounds.

[d] 20% H_2O on wet-gas basis; see ref 9.

Table 12. Range of Critical Compositions in Gas from Paraho Retort by Direct Mode[a]

Component	Amount (dry vol %)		
	High	Low	Mean
CO_2	27.7	18.0	22.8
H_2S	0.55	0.19	0.30
NH_3	1.23	0.50	0.70

[a] Represents 82 sample analyses taken in 1977 and 1978; see ref 8.

2. Description of Process

The modified in-situ process consists of retorting a rubblized column of broken shale, formed by expansion of the oil shale into a previously mined-out void volume. In retort 5 the mined void volume is removed from the retort zone in the form of a vertical slice along the center of the room, extending from the top of the rubble pile to be formed, to the production level. This system is known as a vertical free-face retort system (VFFR). In retort 6 three horizontal levels are mined out similarly to room and pillar mining and then the oil shale is blasted above and below the mined-out sections to the horizontal rooms. This system is the horizontal free-face retort system (HFFR).[13]

After the column of shale has been rubblized, connections are made to both the top and bottom and retorting is carried out (Fig. 2). Retorting is initiated by heating the top of the rubblized shale column with the flame formed from compressed air and an external heat source, such as propane or natural gas. After several hours the external heat source is removed and the compressed air flow is maintained, with the carbonaceous residue in the retorted shale used as fuel to sustain air combustion. In this vertical retorting process the hot gases from the combustion zone move downward to pyrolyze the organic matter in the shale below that zone, producing gases, water vapor, and shale-oil mist, which condense in the trenches at the bottom of the rubblized column. The crude shale oil and by-product water are collected in a sump and pumped to storage. Part of the off-gas is recirculated to control the oxygen level in the incoming air and the retorting temperature. The remainder of the off-gas passes on to the desulfurization train.[10]

3. Basis of Retort Design and Operation

The projected bases for design and operation of Oxidental retorts 7 and 8 are given in Table 13. [14,15] The design basis for retort 6 is also given.

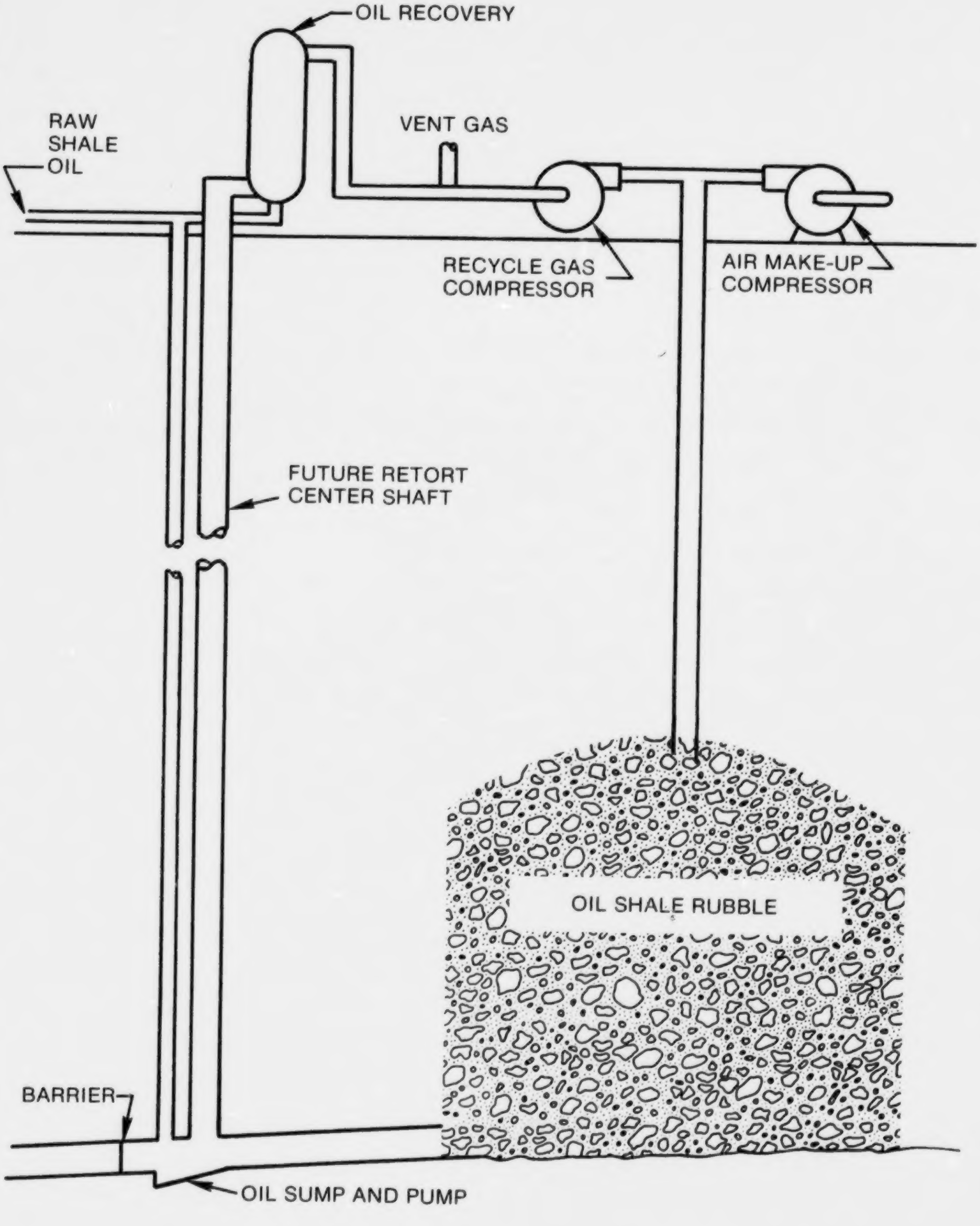

OIL RECOVERY
RAW SHALE OIL
VENT GAS
RECYCLE GAS COMPRESSOR
AIR MAKE-UP COMPRESSOR
FUTURE RETORT CENTER SHAFT
OIL SHALE RUBBLE
BARRIER
OIL SUMP AND PUMP

Figure 2. Flow Diagram of the Occidental Modified In-Situ Process

TYPING GUIDE SHEET

Table 13. Design Basis for Occidental Vertical MIS Retorts

Parameter	Retort 6[a]	Retorts 7 and 8[b]
Retort size (tonnes)	329,058	618,120
Oil-shale assay (ℓ/tonne)	62.5	62.5
Method of retorting	Direct in-situ	Direct in-situ
Gas injected	Air[c]	50% air/50% steam
Gas production rate (sm^3/min)	408	1100
Gas productions ratio (sm^3/tonne)	588	296
Gas ratio, CO_2/H_2S (mole/mole)	330 to 130	165
Heating value, HHV (joules/sm^3)	1.6×10^6 to 2.2×10^6	4.1×10^6
Pressure (psig)	Atmospheric	Atmospheric
Temperature (°C)	57 to 66	57 to 77

[a] See ref 13.

[b] Estimated from Oxy No. 6 and refs 14 and 15.

[c] Steam injected at end of run.

4. Retort-Gas Characterization

The composition of the gas produced by retort 6 at midpoint of the run is given in Table 14. The composition of the gas varied throughout the run. In the initial stage of operation the CO_2/H_2S molar ratio averaged about 330 to 1. After steady-state operation was established, the CO_2/H_2S molar ratio averaged about 165 to 1.[13] Retorts 7 and 8 will be operated using a 50% oil/50% steam mixture injected into the retort. The use of steam will affect the composition of the gas produced. The quantity of COS in the gas is expected to increase.

D. GEOKINETICS HORIZONTAL IN-SITU-RETORT GAS

1. Introduction

Geokinetics is developing the technology of recovering shale oil from shallow formations of oil shale. The method consists of detonating implanted explosives to rubblize the shale. This raises the overburden, thereby developing void spaces among the broken shale. The bed of broken shale (retort) is then ignited with a fuel-air mixture injected at one end, and the retort products are expelled through a production hole at the other end (Fig. 3). The retort burn advances horizontally. When the retort is well ignited, the fuel is shut off and only air is fed to the injection hole.

Retort 18 was fired from November 16, 1979, to February 5, 1980. Retort firings will continue in an effort to develop this technology. The aim of this program is the production of 320 m^3 of oil per day over about a 10-year period from small shallow retorts.

2. Basis of Retort Design and Operation

The design basis for geokinetics retort 18 is given in Table 15.[16,17]

3. Retort Gas Characterization

The average composition of the gases produced by retort 18 is given in Table 16.

Table 14. Gas Produced by Occidental Vertical MIS Retort[a]

Component	Composition	
	(sm³/tonne[b])	(vol %) (DG)[c]
H_2	45.0	7.65
CO	5.2	0.89
CO_2	188.8	32.26
CH_4	8.4	1.44
C_2H_4	0.4	0.07
C_2H_6	1.3	0.224
C_3H_6	0.4	0.0
C_3H_8	0.6	0
C_4	0.6	0
C_5 +	0.1	0.01
H_2S	0.7	0.1
NH_3	c	c
N_2	330.5	56.41
O_2	0.5	0.08
SO_2	0.9	0.15
NO_x	0.2	0.03
CS_2	c	c
RSH	c	c
COS	0.02	(1—40 ppm)
Total, DG	585.9	99.611
H_2O		38.3[d]

[a] Gas produced by Oxy No. 6 at midpoint of run (Jan. 15, 1979); see ref 13.

[b] Average calculated values.

[c] No data.

[d] Wet-gas basis.

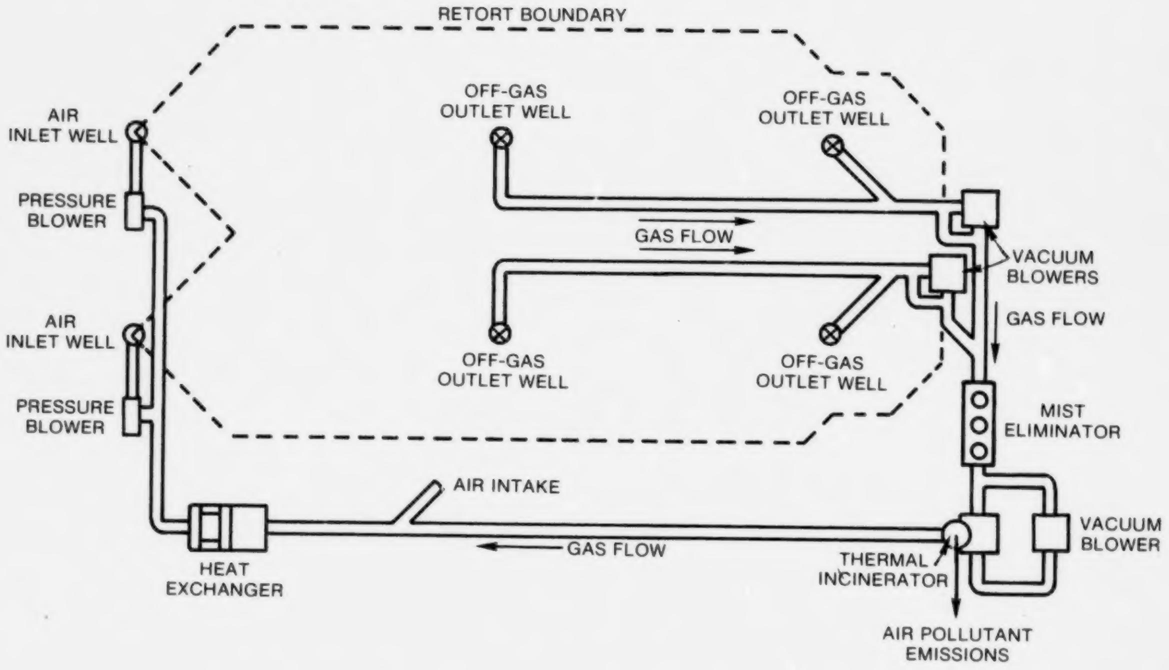

RETORT BOUNDARY
AIR INLET WELL
PRESSURE BLOWER
AIR INLET WELL
PRESSURE BLOWER
OFF-GAS OUTLET WELL
OFF-GAS OUTLET WELL
OFF-GAS OUTLET WELL
OFF-GAS OUTLET WELL
GAS FLOW
VACUUM BLOWERS
GAS FLOW
MIST ELIMINATOR
AIR INTAKE
VACUUM BLOWER
GAS FLOW
HEAT EXCHANGER
THERMAL INCINERATOR
AIR POLLUTANT EMISSIONS

Figure 3. Flow Diagram of Geokinetics Retort No. 17 Off-Gas Handling System

Table 15. Design Basis for Geokinetics Horizontal In-Situ Retort[a]

Retort size (m^3)	10,025[b]
Oil-shale assay (ℓ/tonne)	83.3— 91.6
Method of retorting	Direct in-situ
Gas injected	Air
Gas production rate (sm^3/min)	45.3
Gas production ratio	c
Gas ratio, CO_2/H_2S (mole/mole)	181
Heating value, HHV (joules/sm^3)	3.35×10^6
Pressure (psig)	Atmospheric
Temperature (°C)	54

[a] Gas produced by Geokinetics retort No. 18; see refs 16 and 17.

[b] Retort No. 19 projected at 20,134 m^3.

[c] Data not available.

Table 16. Gas Produced by Geokinetics Horizontal In-Situ Retort[a]

Component	Composition (dry vol %)
H_2	7.47
CO	8.03
CO_2	23.48
CH_4	1.61
C_2H_4	0.085
C_2H_6	0.297
C_3H_6	0.09
C_3H_8	0.13
C_4	0.15
C_{5+}[b]	0.071
H_2S	0.13
NH_3	0.060
N_2	57.4
O_2	1.13
SO_2	c
NO_x	c
CS_2	c
RSH	c
COS	(40 ppm)
Total	100.13
H_2O	15.0[d]

[a] Gas produced by Geokinetics retort No. 18; see ref 16.

[b] C_6 to C_{10} hydrocarbons present but not measured.

[c] No data.

[d] Wet-gas basis.

E. UNION SGR-3 RETORT GAS

1. Introduction

The Union Oil Company of California (Union) have been involved in oil shale activities for more than 50 years. The development of their retorting technology was initiated in the early 1940s, and several variations of a vertical-kiln retorting process, with upward flow of shale and countercurrent downward flow of gases and liquids, have been developed. Two variations are known as retort A and retort B. Union Oil now proposes to construct a 9090 tonnes/day demonstration plant, using the retort-B process, together with all the necessary auxiliary facilities.[10]

2. Description of Process

In the retort-B process (shown in Fig. 4) as the crushed oil shale flows upward through the retort it is met by a stream of hot (510 to 538°C) recycle gas from the recycle gas heater flowing downward. The rising oil-shale bed is heated to retorting remperature by countercurrent contact with the hot recycle gas, resulting in the evolution of the shale-oil vapor and product gas. This mixture of shale-oil vapor and product gas is forced downward by the recycle gas and is cooled by contact with the cold incoming shale in the lower section of the retort cone. The liquid level in the lower section is controlled by withdrawal of the oil product. The recycle and product gases are removed from the space above the liquid level. The product gas is first sent to a venturi scrubber for cooling and removal of heavy hydrocarbons by oil scrubbing. That portion of the product gas not recycled is then sent to the desulfurization train. Before the gas reaches the desulfurization train, it may be compressed and oil-scrubbed to recover additional hydrocarbons.[10]

3. Basis of Retort Design and Operation

The basis for design for the Union SGR-3 retort is given in Table 17.[18,19]

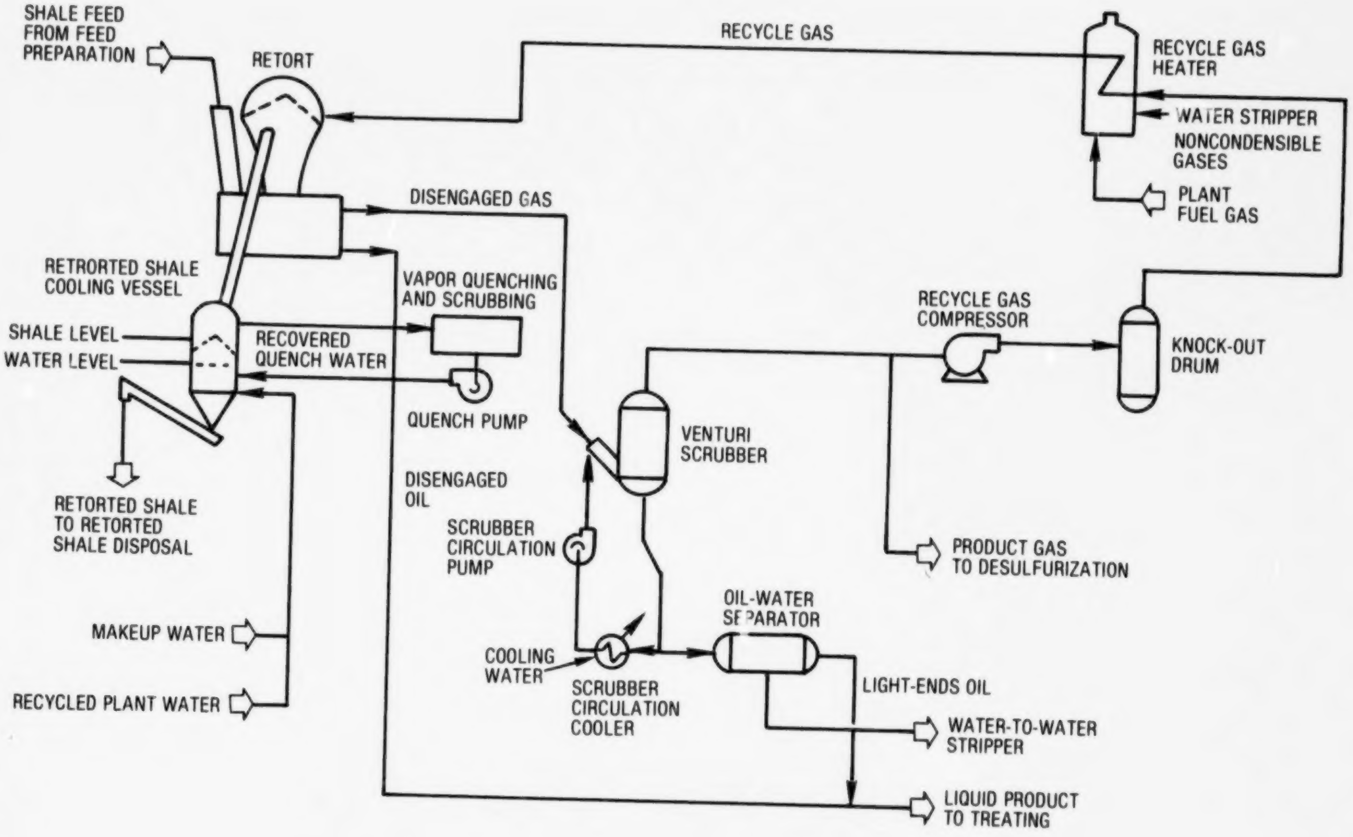

SHALE FEED
FROM FEED
PREPARATION
RETORT
RECYCLE GAS
RECYCLE GAS
HEATER
WATER STRIPPER
NONCONDENSIBLE
GASES
PLANT
FUEL GAS
DISENGAGED GAS
RETORTED SHALE
COOLING VESSEL
VAPOR QUENCHING
AND SCRUBBING
SHALE LEVEL
WATER LEVEL
RECOVERED
QUENCH WATER
QUENCH PUMP
RECYCLE GAS
COMPRESSOR
KNOCK-OUT
DRUM
VENTURI
SCRUBBER
RETORTED SHALE
TO RETORTED
SHALE DISPOSAL
DISENGAGED
OIL
SCRUBBER
CIRCULATION
PUMP
PRODUCT GAS
TO DESULFURIZATION
OIL-WATER
SEPARATOR
MAKEUP WATER
COOLING
WATER
SCRUBBER
CIRCULATION
COOLER
LIGHT-ENDS OIL
RECYCLED PLANT WATER
WATER-TO-WATER
STRIPPER
LIQUID PRODUCT
TO TREATING

Figure 4. Flow Diagram for Retort System in Union Oil Retort B Prototype Plant

Table 17. Design Basis for Union SGR-3 Retort[a]

Shale-oil production	1440 m^3/day[b]
Oil-shale throughput	9090 tonnes/day
Oil-shale assay	157.4 ℓ/tonne
Method of retorting	Indirect mode
Method of heating	Indirect heating of recycled retort gas
Gas production ratio	29.9 sm^3/tonne
Gas production rate	188.7 sm^3/min
Gas mole ratio, CO_2/H_2S	4.35
Heat content, HHV	42.38×10^6 joules/sm^3
Pressure	5—10 psig
Temperature (°C)	65.5—71.1°C

[a] See refs 18 and 19.

[b] Stripped shale-oil production is 1419 m^3/day.

4. Retort Gas Characterization

The estimated composition of the gas that will be produced by the Union SGR-3 retort is given in Table 18.

F. TOSCO-II RETORT GAS

1. Introduction

Tosco II is a process developed by the Oil Shale Corporation (Tosco). Initial development work began in 1955; in 1964 a 909 tonne/day semi-works plant was constructed and tested. A full-scale commercial plant is planned by the Colony Development Operation, a joint venture of several companies who formed or own Tosco.

2. Description of the Process

The heart of the processing sequence is the Tosco-II pyrolysis (retorting) unit and associated oil recovery equipment. The flowsheet for a single unit (or train) is shown in Fig. 5. The raw shale from the final crusher is fed to a fluidized bed, where it is preheated to about 500°F with flue gases from a ball heater. The residual hydrocarbons in the flue gases are burned in the ball heater.[10]

The preheated shale is fed to a horizontal rotating retort (pyrolysis drum), together with approximately 1.5 times its weight in hot ceramic balls from a ball heater in order to raise the shale to pyrolysis temperature (482°C) and convert its contained organic matter to shale-oil vapor. The oil vapors are withdrawn and fed to a fractionator for hydrocarbon recovery. The mixture of balls and spent shale is discharged through a trommel, in order to separate the emerging warm balls from the processed shale.[10]

The warm balls are purged of dust with flue gases from a steam preheater, and the dust is removed from the flue gases by wet scrubbing. The dust-free warm balls are returned to the ball heater via the ball elevator. In the ball heater they are reheated to about 704°C and then recirculated to the pyrolysis drum. The hot spent shale is cooled

Table 18. Gas Produced by Union SGR-3 Indirect-Heated Retort[a]

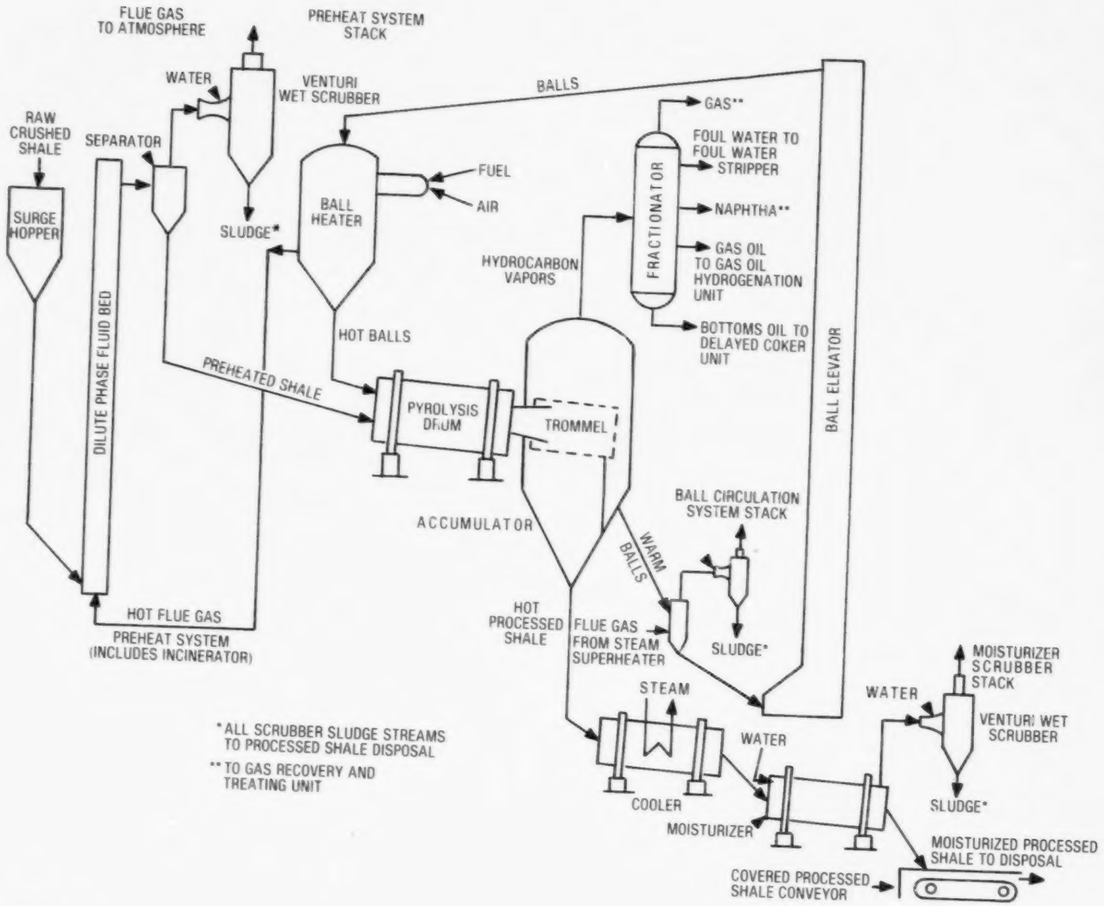
Component	Amount	
	(sm^3/tonne)	(dry vol %)
H_2	6.95	23.34
CO	1.44	4.85
CO_2	4.95	16.62
CH_4	6.63	22.28
C_2H_2	0.06	0.19
C_2H_4	0.51	1.72
C_2H_6	2.28	7.67
C_3H_6	1.13	3.81
C_3H_8	b	b
C_4H_6	1.02	3.43
$i\text{-}C_4H_8$	0.09	0.29
$n\text{-}C_4H_8$	0.79	2.66
$i\text{-}C_4H_{10}$	0.34	1.14
$n\text{-}C_5H_8$	0.09	0.29
$i\text{-}C_5H_8$	0.12	0.39
C_5H_{10}	0.06	0.19
C_5H_{12}	0.28	0.94
C_{6+}	1.84	6.19
H_2S	1.14	3.82
NH_3	b	b
N_2	0.03	0.11
O_2	c	c
SO_2	–	(125 ppm)
NO_x	b	b
CS_2	–	(20 ppm)
RSH	–	(164 ppm)
COS	0.02	(542 ppm)
Total, DG	29.77	100.00
H_2O	5.95	20[d]

[a] Oil assay, 157ℓ/tonne; see ref 19.

[b] No data.

[c] No data; likely nil.

[d] Estimated value, wet-gas basis.


FLUE GAS TO ATMOSPHERE
PREHEAT SYSTEM STACK
WATER
VENTURI WET SCRUBBER
BALLS
RAW CRUSHED SHALE
SEPARATOR
SURGE HOPPER
SLUDGE*
BALL HEATER
FUEL
AIR
GAS**
FOUL WATER TO FOUL WATER STRIPPER
NAPHTHA**
GAS OIL TO GAS OIL HYDROGENATION UNIT
BOTTOMS OIL TO DELAYED COKER UNIT
FRACTIONATOR
HYDROCARBON VAPORS
DILUTE PHASE FLUID BED
HOT BALLS
PREHEATED SHALE
PYROLYSIS DRUM
TROMMEL
BALL ELEVATOR
ACCUMULATOR
BALL CIRCULATION SYSTEM STACK
WARM BALLS
HOT FLUE GAS
PREHEAT SYSTEM (INCLUDES INCINERATOR)
HOT PROCESSED SHALE
FLUE GAS FROM STEAM SUPERHEATER
SLUDGE*
MOISTURIZER SCRUBBER STACK
STEAM
WATER
VENTURI WET SCRUBBER
WATER
COOLER
MOISTURIZER
SLUDGE*
MOISTURIZED PROCESSED SHALE TO DISPOSAL
COVERED PROCESSED SHALE CONVEYOR

*ALL SCRUBBER SLUDGE STREAMS TO PROCESSED SHALE DISPOSAL

**TO GAS RECOVERY AND TREATING UNIT

Figure 5. Flow Diagram for Pyrolysis and Oil Recovery Unit TOSCO-II Process

to about 149°C in a rotating drum cooler and moisturized with water recovered from the plant's foul-water stripper unit.[10]

Unlike some U.S. oil-shale facilities, the Tosco-II/Colony commercial plant will be designed not only to produce shale oil but also to upgrade it on-site to produce synthetic crude oil and liquid petroleum gas (LPG), with ammonia, sulfur, and coke produced as by-products. The shale-oil hydrocarbon vapors from the pyrolysis drum are separated into water, gas, naphtha, gas oil, and bottom oil in a fractionator. The water is sent to a foul-water stripper, the gas and naphtha are sent to a gasoline recovery and treating unit, the gas oil is sent to a hydrogenation unit, and the bottoms oil is sent to the delayed coking unit.[10]

3. Basis of Retort Design and Operation

The basis for design and operation of the Tosco-II retort is given in Table 19.[20,21]

4. Retort Gas Characterization

The average composition of the gas produced by the Tosco-II retort is given in Table 20.[22]

Table 19. Design Basis for Tosco-II Retort[a]

Shale-oil production	8,872 m^3/day[b]
Oil-shale throughput (6 retorts)	60,000 tonnes/day
Oil-shale assay	158 ℓ/tonne
Method of retorting	Indirect mode
Method of heating	Pyrolysis by heated balls
Gas production ratio	38.5 sm^3/tonne[c]
Gas production rate (single retort)	267.6 sm^3[c]
Gas mole ratio, CO_2/H_2S	4.95
Heat content, HHV	35.26×10^6 joules/sm^3[d]
Pressure	Slightly positive
Temperature	60°C

[a] See refs 20 and 21.

[b] Based on pilot study; see ref 21. Production as low sulfur distillate is 7,360 m^3/day; see ref 20.

[c] Calculated from data in ref 21.

[d] Calculated valve based on C_5 and higher MW hydrocarbons removed.

Table 20. . Net Gas Produced by Tosco-II Retort[a]

Component	Amount	
	(sm^3/tonne)	(dry vol %)
H_2	7.74	20.2
CO	1.31	3.40
CO_2	7.83	20.38
CH_4	7.75	20.2
C_2H_2	b	b
C_2H_4	3.21	8.39
C_2H_6	2.91	7.61
C_3H_6	2.73	7.14
C_3H_8	1.28	3.35
C_4	2.00	5.22
C_5	c	c
H_2S	1.58	4.12
NH_3	d	d
N_2	b	b
O_2	b	b
SO_2	b	b
NO_x	b	b
CS_2	Nil[e]	Nil[e]
RSH	-	(35 ppm)
COS	-	(135 ppm)
Total	38.38	100
H_2O	9.59	20[b]

[a] See ref 21.

[b] None reported.

[c] Reported in oil recovered.

[d] Absorbed in water phase and does not appear in gas.

[e] See ref 22.

[f] Wet-gas basis.

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

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IV. REVI[illegible] SULFUR REMOVAL PROCESSES

A. TREATMENT TECHNIQUES

The class of processes that remove sulfurous compounds and carbon dioxide from gases is generically called acid-gas removal or gas-sweeting processes. Removal of acid gases and/or other gaseous impurities from gas streams is accomplished by chemical conversion to another compound, by absorption into a liquid, or by adsorption on a solid.

In the first method the gas is passed through a fixed bed or is contacted with a liquid, whereby the impurities are converted to another compound that can be more easily removed. Conversion is either by direct chemical reaction with the bed or liquid or by catalytic reaction.

In the second method the gas stream is contacted with a liquid, and the gaseous impurities are either chemically or physically dissolved in the liquid absorbent. The absorbent is subsequently regenerated to strip the absorbed gas and is then recycled.

When the method of adsorption is used on a solid, the gas is passed through a fixed bed of granulated solid material. The impurities are adsorbed and held by the solid adsorbent. When the bed becomes saturated, it is replaced or regenerated.

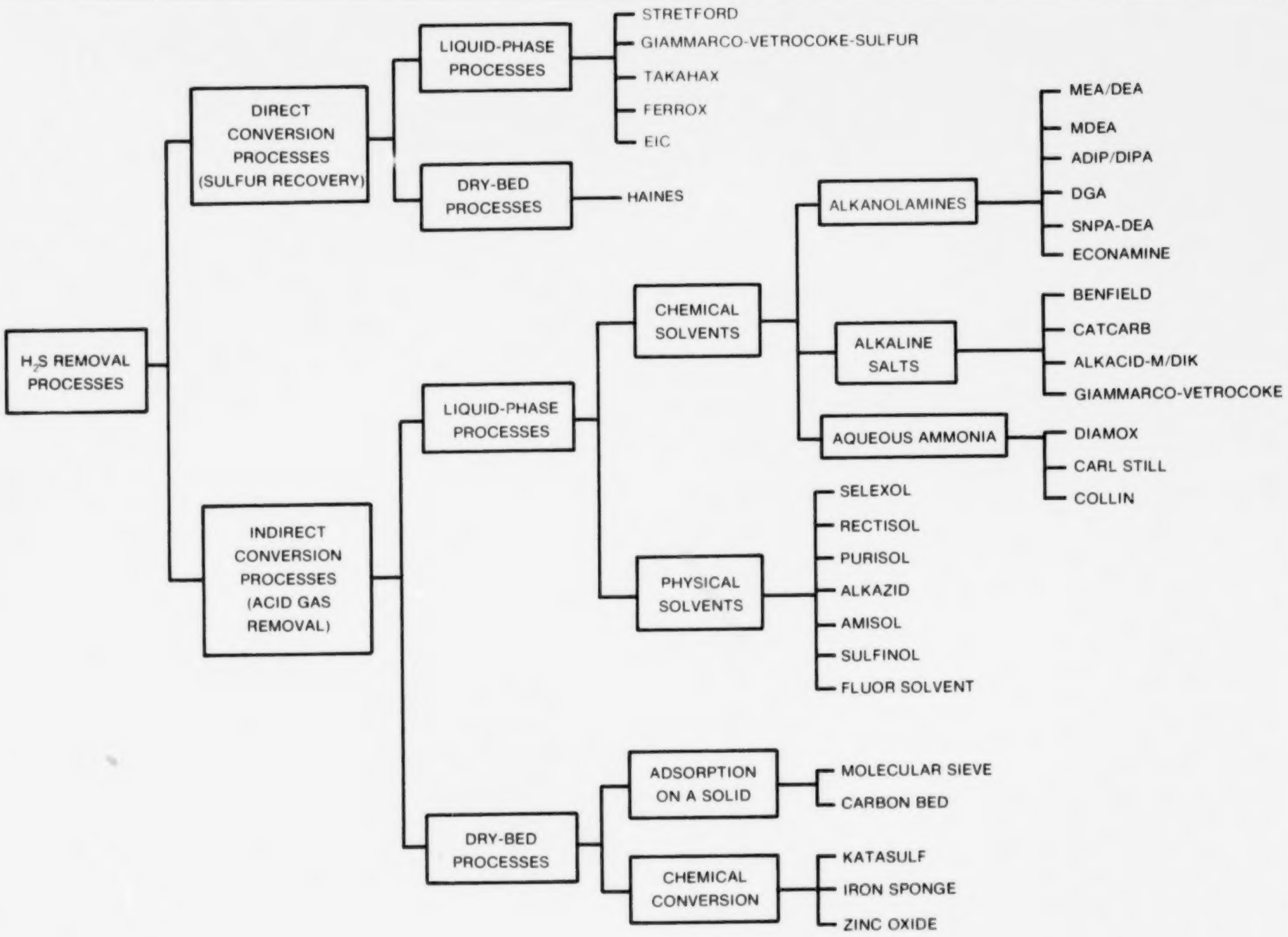
Numerous processes for removal of sulfur compounds have been developed from these methods and more than 30 of them have achieved commerical importance. Each commercial process has specific advantages, disadvantages, or limitations and was developed to satisfy specific needs. Some processes are designed to remove both H_2S and CO_2, whereas other processes are more selective toward H_2S or CO_2 removal. All liquid-phase processes will remove CO_2 to some degree, along with the H_2S. Some processes are economical for only bulk removal of acid gas and will not achieve a high degree of acid-gas removal. Other processes will achieve a high degree of acid-gas removal, to the ppm level, but are not economical for gases containing large amounts of acid gases. Still other processes are effective only if the CO_2/H_2S ratio is small, whereas others are more effective if the CO_2/H_2S ratio is high. Some processes cannot be used at a low pressure, but some are equally effective at all pressures. Most processes must be carried out at near-ambient temperatures; others require cooling or chilling of the feed gas; some can be used at elevated temperatures, whereas others must be used at elevated temperatures.

All H_2S removal processes can be divided into the general categories of direct- and indirect-conversion processes. In the direct-conversion processes the sulfur compounds are directly oxidized to elemental sulfur or another compound that can be separated and recovered. In the indirect conversion processes the acid-gas components are removed from the feed gas and recovered as a separate stream, which is subsequently processed for recovery of the sulfur. Sulfur is recovered from the concentrated acid-gas stream by the Claus sulfur recovery process or by one of the direct-conversion processes. Both these categories can be further broken down into either gas-phase dry-bed processes or liquid-phase (wet) processes (see Fig. 6).

1. Direct-Conversion Processes

a. Dry Bed—Several dry-bed processes have been described for direct removal of H_2S from hydrocarbon gases based on the classic Claus reaction of H_2S and SO_2 to form elemental sulfur.[1] The application of these processes is limited because of possible plugging of the beds by condensable hydrocarbons and/or other impurities in the gas. None of these processes are known to have achieved commercial importance.

The Claus process, while a dry-bed process, is not in the true sense a gas-treating or sulfur-removal process and therefore is not included in this discussion. The Claus process is used to recover sulfur from hydrocarbon-free acid-gas streams containing large amounts of H_2S and is discussed in Sect. IV-B.



H_2S REMOVAL PROCESSES
DIRECT CONVERSION PROCESSES (SULFUR RECOVERY)
LIQUID-PHASE PROCESSES
STRETFORD
GIAMMARCO-VETROCOKE-SULFUR
TAKAHAX
FERROX
EIC
DRY-BED PROCESSES
HAINES
INDIRECT CONVERSION PROCESSES (ACID GAS REMOVAL)
LIQUID-PHASE PROCESSES
CHEMICAL SOLVENTS
ALKANOLAMINES
MEA/DEA
MDEA
ADIP/DIPA
DGA
SNPA-DEA
ECONAMINE
ALKALINE SALTS
BENFIELD
CATCARB
ALKACID-M/DIK
GIAMMARCO-VETROCOKE
AQUEOUS AMMONIA
DIAMOX
CARL STILL
COLLIN
PHYSICAL SOLVENTS
SELEXOL
RECTISOL
PURISOL
ALKAZID
AMISOL
SULFINOL
FLUOR SOLVENT
DRY-BED PROCESSES
ADSORPTION ON A SOLID
MOLECULAR SIEVE
CARBON BED
CHEMICAL CONVERSION
KATASULF
IRON SPONGE
ZINC OXIDE

Figure 6. Gas-Sweetening Processes

b. **Liquid-Phase Direct-Conversion Processes**—Liquid-phase direct-conversion processes usually are best suited to gases containing low concentrations of H_2S, especially in the presence of substantial concentrations of CO_2. Very little CO_2 is absorbed by the solution, and thus the processes selectively remove the H_2S. The principal disadvantage is the relatively low capacity of the solutions for H_2S, which results in large liquid circulation rates and requires large equipment for separating and processing precipitated sulfur. Generally plants of this type are not economical when the sulfur production rate exceeds 9 tonnes per day. Another disadvantage is that the considerable reaction heat generated by oxidation of H_2S has to be dissipated at low temperature and cannot be recovered.[2] The quality of sulfur produced is lower than that of the sulfur obtained with the indirect processes, and the wastewater from purge streams is a major problem.

Direct-conversion liquid processes have substantial economic advantages over direct-conversion dry-bed processes in that they require less space, eliminate the high cost of bed replacement, and produce higher quality sulfur. Some liquid processes are capable of producing a treated gas of high purity equal to that obtained with dry-bed processes.

2. Indirect-Conversion Processes

a. **Dry Bed**—The dry-bed indirect-conversion processes are generally applied on a batch-loaded basis, where the bed is removed from service when it is loaded and the sorbent is replaced or regenerated. The dry-bed processes are selective for H_2S and generally achieve a high degree of removal. These processes are limited to the treatment of gas streams of small volume or to gas streams containing relatively low amounts of sulfur compounds. Regeneration of the bed is only partly achieved, and the bed eventually becomes plugged with sulfur and must be replaced. The economics generally limit application of these processes to plants recovering less than 10 tons of sulfur per day.[3]

The advantages of dry-bed processes are simplicity, low cost, and ease of operation. Essentially complete removal of H_2 can be achieved, and some processes will selectively remove H_2S without removing any CO_2. The disadvantages are the large space requirements for the equipment, high maintenance costs for bed replacement, and problems with sulfur recovery.

b. Liquid-Phase Process Involving Chemical Solvents——Chemical solvents involve absorption by reversible chemical reaction of the H_2S with a water solution of the absorbent. The following three types of chemical solvents are used:

Alkanolamines——Many types of alkanolamines are used as absorbents (Fig. 6), and numerous processes and variations of them have been applied, depending on the physical conditions of the gas to be treated, its composition, and its purity requirements. Generally alkanolamine processes exhibit high reactivity with H_2S and achieve a high degree of removal. The processes are not sensitive to pressure, and operate at near-ambient temperatures. Organic sulfur compounds are removed to some extent, but the lighter molecular weight amines may form nonregenerative compounds when absorbing organic sulfur or cyanide compounds. The lighter amines, though less expensive and capable of higher absorption capacity, are not selective in absorbing H_2S, present corrosion problems in stripper and heat-exchanger surfaces, and are plagued by higher solvent vaporization losses than are the heavier amines. Alkanolamine processes are generally preferred for treatment of gases containing moderate amounts of acid gas at near-ambient temperature and pressure.

Alkaline salts——Alkaline salt processes employ an aqueous solution of a potassium or sodium salt that forms a buffered solution with a pH of about 9 to 11. The weak alkaline solution chemically absorbs the acid-gas components. These processes are of two types: those carried out at low (ambient) temperature and pressure and those carried out at elevated temperature and pressure. The low-pressure processes have given way to more efficient processes and are not currently used. The hot processes have an advantage when the feed gas is hot (up to 149°C) and under pressure (<100 psig). Stripping is accomplished partly by flashing, and thus the energy required for regeneration is lower than that for amine systems. The alkaline salt solution does not degrade significantly, and only minimum purge and makeup are required. Organic sulfur compounds are removed by the process, and it can be made partly selective toward H_2S removal. The alkaline salt processes are usually the best ones to use when bulk removal of CO_2 is required.

Aqueous ammonia—Aqueous ammonia processes are generally applied when the gas to be treated contains ammonia. The ammonia contained in the gas is absorbed simultaneously with the H_2S and thus serves as the active agent in the absorber solution. No chemical additives are required. Ammonia can be recovered in addition to the acid-gas components. Under certain operating conditions H_2S can be selectively removed. Removal of up to about 97% of the H_2S can be achieved; however, organic sulfur compounds are only partly absorbed.

c. Liquid-Phase Processes Involving Physical Solvents—Physical-solvent processes are based on H_2S, CO_2, and minor gas impurities being more soluble in certain anhydrous organic solvents than are the fuel-gas components, i.e., hydrocarbons and hydrogen. Since their solubilities increase with pressure, the processes generally require high pressure to be economical. The solvent is regenerated by pressure reduction, gas stripping, or heat applied to produce a concentrated stream of absorbed gas.

Most physical solvents have higher solubility for H_2S than for CO_2, and a high degree of selectivity can be obtained with some processes. The solubility of hydrocarbons, however, increases with molecular weight. Consequently hydrocarbons above C_4 are also largely removed with the acid gas.

The advantages of physical solvents over chemical solvents are lower heat and power consumption, greater removal of organic sulfur components, higher selectivity for H_2S, no purge or wastewater streams, and little corrosion. The disadvantages are that a high-feed gas pressure is required, heavier hydrocarbons are absorbed, the solvent loss is high, and the solvent cost is high.

Physical-solvent processes are most economical when the feed gas is available at high pressure. These processes are usually used for bulk removal of acid-gas constituents when the acid-gas impurities make up an appreciable fraction of the total gas stream, making the cost of removing them by heat-regenerable chemical solvents less attractive. When high-purity treated gas is required, additional solvent regeneration steps beyond simple flashing are required.

B. PROCESS FOR RECOVERING SULFUR

The Claus sulfur process is the principal process used for recovery of sulfur from acid gases produced by the indirect-conversion processes. The Claus process is discussed in some detail since it is important that the operation, capabilities, and limitations of the process be understood before fuel gas desulfurization processes are described.

A flow diagram of a conventional Claus system is shown in Fig. 7. The basic Claus reaction is

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

The conventional process is carried out in stages: the first stage is at high temperature in a thermal oxidation furnace, where one-third of the H_2S is combusted to SO_2 in the presence of air; the reaction in the succeeding stages occurs at lower temperatures in the vapor phase by catalytic oxidation. Usually two or more catalytic stages are employed. Sulfur is recovered after each stage by the gas streams being cooled and condensed. The gas is then reheated to the operating temperature of the succeeding stage. When the acid-gas feed is mostly

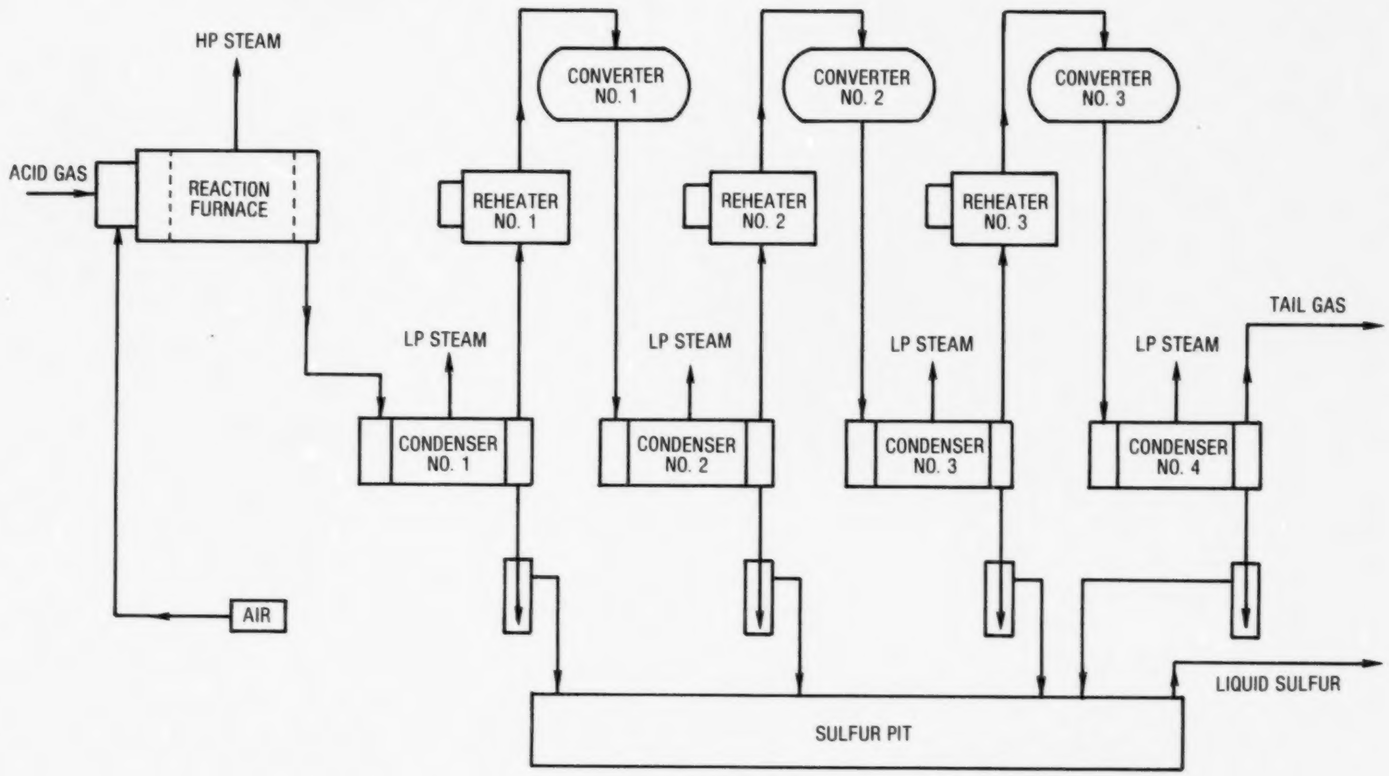

HP STEAM
ACID GAS
REACTION FURNACE
AIR
CONVERTER NO. 1
CONVERTER NO. 2
CONVERTER NO. 3
REHEATER NO. 1
REHEATER NO. 2
REHEATER NO. 3
LP STEAM
LP STEAM
LP STEAM
LP STEAM
TAIL GAS
CONDENSER NO. 1
CONDENSER NO. 2
CONDENSER NO. 3
CONDENSER NO. 4
LIQUID SULFUR
SULFUR PIT

Figure 7. Typical Three-Stage Claus Process

H_2S, sulfur conversions of up to 70%[4] can be obtained by the thermal oxidation step alone, and overall conversions of up to 99%[5] have been obtained by use of four catalytic stages. The average sulfur recovery yield obtained with properly designed and operated systems usually ranges from 93—97%.[6] The remaining 3 to 7% of the sulfur is present in the Claus unit off-gas.

Recent developments have improved the process so that sulfur recovery levels of above 99% are routinely achieved by employing tail-gas treatment;[5] acid-gas streams containing as little as 5% H_2S have been processed with modified Claus systems.[7]

A necessary condition for successful operation of the thermal oxidation furnace is that the acid-gas mixture be rich enough (high in H_2S content) to ensure stable combustion at the required reaction temperature. The gas stream entering the first-stage catalytic converter should be at its stoichiomatic ratio of 2 parts of H_2S to 1 part of SO_2 and be free of oxygenated impurities (SO_3), unburned heavy hydrocarbons, soot, and excessive ammonia. An imbalance of either H_2S or SO_2 will cause the excess component to pass through the system unreacted. Oxygen causes sulfonation of the catalyst, which results in loss of catalyst activity. Soot and carbonaceous material and ammonia, through formation of ammonium sulfate, cause the catalyst beds to become plugged. Unburned hydrocarbons that condense and stick to the catalyst will also cause loss of catalyst activity.

The operating temperature required for the thermal oxidation furnace is largely governed by the impurities in the acid gas. If the acid gas consists of H_2S, COS, CS_2, and CO_2, a furnace temperature of 700 to 800°C is sufficient. If the gas contains hydrocarbon compounds, ammonia, and other combustible impurities, temperatures of 1000 to 1200°C are required to assure complete combustion of the impurities and elimination of soot formation. The presence of combustible impurities in the acid gas increases the amount of air that must be introduced to the combustion chamber, and their products of combustion greatly add to the quantity of process gas entering the catalytic stages.

1. Methods for Processing Acid Gases Containing 16 to 100% H_2S

If the acid gas contains 50 to 100% H_2S, the total volume of acid gas is normally fed to the combustion chamber (the classic, or the straight-through, process). The amount of air fed to the reaction furnace is controlled to combust one third of the H_2S and all the ammonia and hydrocarbon impurities in the feed. If the temperature is maintained at the proper level (1000 to 1100°C), organic impurities are oxidized and the catalytic stages operate without significant problems. As the H_2S content of the acid gas decreases, the lower the temperature obtained in the reaction furnace becomes. Longer residence time in the furnace is required to compensate for this lowered temperature, and thus larger chamber volumes are needed to maintain the dyanmic equilibrium. Below 35% H_2S, the combustion required to produce the SO_2 for the Claus reaction is no longer possible without special modifications being employed.

Below 50% H_2S, the Claus process is usually modified. If the H_2S content is between 16 and 50%, the split-flow process is often applied. With this process only one-third of the acid gas is fed to the thermal oxidation furnace. Stable combustion is obtained by the H_2S being completely combusted to SO_2. The other two-thirds of the acid gas bypasses the furnace and is mixed with the gases from the thermal oxidizer before they enter the first catalytic converter. However, impurities in the acid-gas stream are detrimental to the downstream catalytic section of the Claus plant and can affect the service life of the catalyst and the purity of the sulfur produced. If impurities are present in the acid gas, the complete stream should be fed to the combustion chamber as in the straight-through process. Preheating the combustion air and/or acid-gas stream or burning supplemental fuel or sulfur will enable stable combustion to be obtained.

2. Methods for Processing Acid Gases Containing Less Than 16% H_2S

If the acid gases contain less than 16% H_2S (called lean acid gases), the methods for obtaining stable combustion involve the following processes:

a. Preheating Process——The acid gas and/or combustion air is preheated before it enters the thermal oxidizer. Preheating is accomplished by heat exchange with the hot gases exiting the combustion chamber, by steam or by externally fired heaters. Only a limited amount of heat can be obtained by preheating. For lean acid gases it may be nessary to use supplemental fuel in direct-fired burners. However, burning the fuel adds to the cost of operation and to the volume of gases that must be handled by the downstream components.

b. Sulfur Burning—By-Pass Process——The Claus thermal oxidizer as such is eliminated. The SO_2 required for the reaction is obtained by burning liquid sulfur in a separate combustion chamber. This has the advantage that stable combustion is obtained in the sulfur burner and that the gas produced is mostly SO_2, depending on the purity of sulfur burned. Off-grade sulfur can be burned since the carbonaceous material is oxidized to carbon dioxide and water. The acid-gas stream is preheated in a gas-fired heater. The hot acid gas and the SO_2 from the sulfur burner are then mixed and fed to the catalytic converter. Application of this process is limited to relatively pure acid gases since even small quantities of hydrocarbon can cause carbon and tar to deposit on the catalyst and/or the sulfur quality to be degraded.

c. Oxygen Process——Oxygen in place of air is used in the thermal oxidizer. This eliminates the ballasting effect of the nitrogen; thus less heat is required to maintain equilibrium and the volume of gases passing to the catalytic stages is reduced. Depending on the quantity of combustible material in the feed, oxygen is mixed to the acid gas or to a portion of the acid gas, which is then fed to one or more burners. If insufficient heat is generated because of lean-acid-gas mixtures, the supplemental fuel must be burned.

d. Sulfur Burning—Straight-Through Process——A portion of the acid gas is mixed with excess air, depending on the quantity of combustible impurities in the acid gas, and is then fed to a special burner. The remaining acid gas is fed into the combustion chamber. Liquid sulfur is burned in a special burner to supply most of the SO_2 required for the Claus reaction and the heat required to stablize the combustion process. The quantity of sulfur burned is limited since the $H_2S:SO_2$ ratio of 2:1 must be maintained. Supplemental fuel may have to be used if the heat input is insufficient for thermal equilibrium to be maintained in the furnace.

3. Cost Data

Table IV-1 gives the relative capital and operating costs of the various process options, based on cost data reported by Fischer.[8] The sulfur-burning by-pass process results in the lowest capital and operating costs of all processes available for processing lean acid gases. However, its application is limited to relatively hydrocarbon-free acid gases. When the H_2S and hydrocarbon contents are low, the oxygen process is preferable provided that the oxygen can be obtained at low cost. The preheating process is used for those applications in which the acid gas contains hydrocarbon impurities and the H_2S content is moderately low.

The sulfur-burning straight-through process is the most expensive process. Since the entire gas stream is introduced to the combustion chamber, its temperature must be raised to the furnace operating temperature. The higher the furnace operating temperature, the higher the operating cost and the larger the equipment required.

4. Claus Tail-Gas Treatment Processes

The tail gas from a properly designed and operated Claus sulfur recovery plant may contain from 8,000 to 28,000 ppmv of sulfurous compounds (H_2S, SO_2, COS, CS_2, S vapor).[6] In order to comply with the more stringent current regulations, many processes have been developed to clean up Claus tail gases.

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Table 21. Comparison of Claus Process Options[a]

Option	Relative Gas Volume[b]			Relative Capital Cost			Relative Operating Cost		
	At 900°C	At 1000°C	At 1100°C	At 900°C	At 1000°C	At 1100°C	At 900°C	At 1000°C	At 1100°C
Sulfur burning—by-pass process	1.00[c]			1.00[c]			1.00[c]		
Oxygen process	0.98	1.06	1.13	1.66	1.97	2.50	1.26	1.50	1.92
Preheat process	1.32	1.53	1.91	1.77	2.06	2.56	1.80	2.11	2.62
Sulfur burning—straight-through process	1.69	1.96	2.45	2.16	2.59	3.13	1.95	2.34	2.82

[a] Based on cost data reported in ref 8.

[b] Gas volume to first catalytic reactor for feed gas containing 8% H_2S.

[c] Thermal oxidizier stage eliminated; gas is indirectly heated only to operating temperature of first catalytic stage.

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Figure 8 shows the principal Claus tail-gas treatment processes. Three basic approaches to tail-gas cleanup are employed. With the first approach all sulfurous compounds are reduced to H_2S in a high-temperature catalytic converter. The gas is then cooled and the condensed water removed. After the H_2S is cooled, it is either absorbed and subsequently regenerated as a concentrated acid-gas stream for recycle back to the Claus unit or is reacted and recovered as elemental sulfur. With the second approach all sulfurous compounds are oxidized to SO_2 in a thermal oxidation furnace. The SO_2 is then either absorbed and subsequently regenerated as a concentrated SO_2 gas stream for recycle back to the Claus unit or is reacted to form another compound, which is then recovered as by-product. The third approach is to extend the Claus reaction at lower temperatures. When a catalytic system is operated at a lower temperature than normal (near or below the sulfur condensation temperature), the thermodynamic equilibrium for the formation of sulfur from H_2S and SO_2 is further enhanced. Processes based on this approach are carried out in either the liquid phase with a catalyst present or a gas phase, in which a solid catalyst bed is used.

The choice of which tail-gas treatment process to use depends on many factors, principally those given below:

1. the composition and volume of the tail gas,
2. whether the system can be integrated as part of a new installation or whether it is an add-on to an existing Calus plant,
3. the initial investment cost and/or the operating costs,
4. the utilities required, the sulfur product produced, and/or the wastes produced,
5. the performance, reliability, and operating range of the system.

The Shell Claus off-gas treating (SCOT) process, the Beavon sulfury recovery process (BSRP), and the Wellman-Lord (W-L) process are the most widely applied processes. If the tail gas is low in CO_2, the SCOT process usually produces the best economics of the three. If the gas

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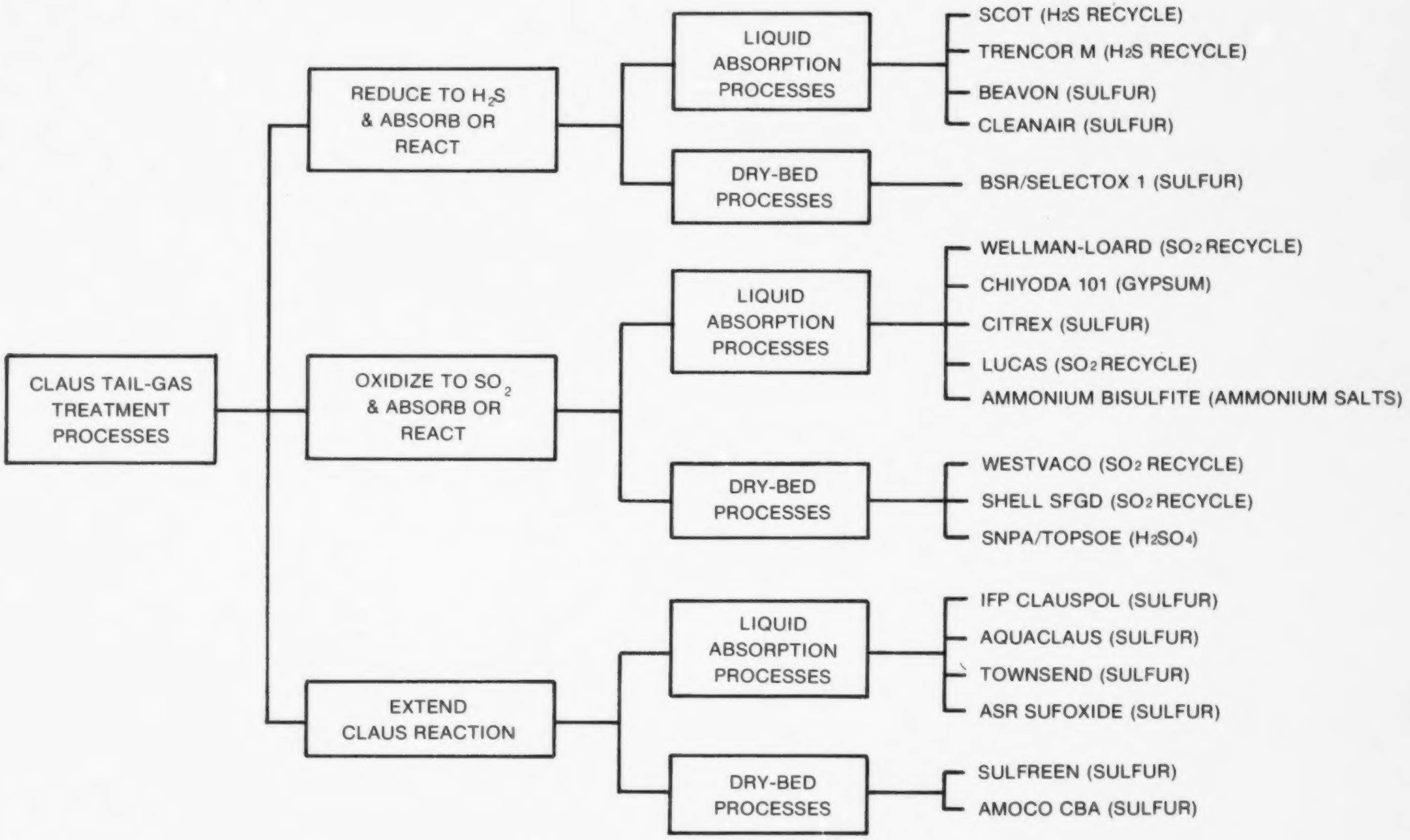
CLAUS TAIL-GAS TREATMENT PROCESSES
REDUCE TO H_2S & ABSORB OR REACT
OXIDIZE TO SO_2 & ABSORB OR REACT
EXTEND CLAUS REACTION
LIQUID ABSORPTION PROCESSES
DRY-BED PROCESSES
SCOT (H_2S RECYCLE)
TRENCOR M (H_2S RECYCLE)
BEAVON (SULFUR)
CLEANAIR (SULFUR)
BSR/SELECTOX 1 (SULFUR)
LIQUID ABSORPTION PROCESSES
DRY-BED PROCESSES
WELLMAN-LOARD (SO_2 RECYCLE)
CHIYODA 101 (GYPSUM)
CITREX (SULFUR)
LUCAS (SO_2 RECYCLE)
AMMONIUM BISULFITE (AMMONIUM SALTS)
WESTVACO (SO_2 RECYCLE)
SHELL SFGD (SO_2 RECYCLE)
SNPA/TOPSOE (H_2SO_4)
LIQUID ABSORPTION PROCESSES
DRY-BED PROCESSES
IFP CLAUSPOL (SULFUR)
AQUACLAUS (SULFUR)
TOWNSEND (SULFUR)
ASR SUFOXIDE (SULFUR)
SULFREEN (SULFUR)
AMOCO CBA (SULFUR)

Figure 8. Claus Tail-Gas Treatment Processes

contains large amounts of CO_2, the W-L or the BSRP may be the best choice.

An excellent discussion of the various Claus tail-gas treating processes is given in a paper presented by Goar at the Fifty-Seventh Annual Convention of the Gas Producers Association.[6]

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8. H. Fischer, "Sulfur Costs Vary with Process Selection," Hydrocarbon Processing 58(3), 125—129 (March 1979).

*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

V. FACTORS INFLUENCING CHOICE OF PROCESS

In selecting a gas-treating process to remove sulfur compounds many factors have to be considered. The most important are the following:

1. the product-gas specifications,
2. the quantity of acid-gas components (CO_2 and H_2S) contained in the gas,
3. the influence of impurities such as COS, CS_2, mercaptans (RSH), NH_3, and HCN,
4. the quantity of heavier hydrocarbons in the gas,
5. the condition of the feed gas (temperature and pressure),
6. the capital and operating costs of the process.

A. PRODUCT-GAS SPECIFICATIONS

1. Sulfur Compounds

Sulfur compounds are removed to prevent air pollution by SO_2 when the gas is combusted. They are also removed for safety and to prevent corrosion and odor problems. For natural-gas distributed by pipeline the total sulfur content is reduced 4.6 grams, or less, per 100 m^3 of gas. If the gas is used as chemical feed stock, sulfur compounds often have to be reduced to less than 1 ppm to protect sensitive catalyst systems.

Generally the cost of removing the sulfur increases as the degree of removal required increases. Achieving a high degree of removal often requires sacrificing other desirable process features, such as H_2S selectivity, process simplicity, or favorable operating economics. The higher the degree of sulfur removal required the more limiting the process selection becomes.

2. CO_2

Carbon dioxide and inert gases have no harmful effect other than that of reducing the heating value of the gas. Often CO_2 can be tolerated and does not have to be removed.

3. COS, CS_2, and RSH

Carbonyl sulfide, carbon disulfide, and mercaptans contribute to the total sulfur content of the gas and generally must be removed to the same degree as H_2S.

4. Dew Point

In a saturated gas a drop in temperature or an increase in pressure will cause water to be condensed in the lines. Therefore the gas should be precooled to the lowest temperature to be encountered in the system. Similarly, condensable hydrocarbons could condense out if the gas conditions dropped below their condensation point.

5. NH_3

If not removed, ammonia could be a problem in that NO_x compounds could be formed when the gas is combusted. Also, ammonia could be detrimental to some desulfurization processes.

B. ACID-GAS COMPONENTS

The most important factor in choosing a gas-treating process is the quantity of acid-gas components, CO_2 and H_2S, contained in the gas and the volume ratio between these two components. If the total quantity of sulfur contained in the gas is small, less than 9 tonnes/day, a dry-bed or direct-oxidation process may be more economical. If the quantity of sulfur is greater than 9 tonnes/day, an indirect process may be more economical.

Although the Claus process is preferable for recovering sulfur from concentrated acid-gas streams produced by indirect processes, it requires an acid-gas feed containing greater than 15% H_2S for effective operation. The higher the concentration of H_2S in the acid gas the more effective the Claus system will be.

Since all liquid-phase indirect processes absorb some CO_2 along with the H_2S, an indirect process selective toward H_2S should be used if the CO_2/H_2S ratio in the feed gas is greater than 1 and is essential if the ratio is greater than 6. If it is necessary to remove the CO_2 along with the H_2S, when the CO_2/H_2S ratio is high, a process selective toward H_2S removal should be used followed by a process that can remove bulk quantities of CO_2. If the acid-gas stream contains less than about 5% H_2S, it is usually more economical to process the acid-gas stream by a liquid-phase direct-oxidation process than by the Claus process.

C. INFLUENCE OF IMPURITIES

Most direct-recovery processes will not remove COS or CS_2 and will only partly remove mercaptans. The alkanolamine processes will remove organic sulfur compounds, but the lighter alkanolamines (MEA) and to some extent DEA form nonregenerable thiosulfates, which degrade the solvent when COS or CS_2 is present in the feed gas. Most alkaline salt processes remove COS and CS_2 by hydrolyzing them to H_2S, but mercaptans are only slightly absorbed. The physical-solvent processes effectively absorb organic sulfur compounds.

If ammonia is not removed before the acid-gas absorption step, it will be absorbed with most processes and end up in the acid-gas stream. Most ammonia in the gas can be removed with the condensates in the precooling step. Small amounts of ammonia can be tolerated by the Claus unit if the quantity of ammonia is small compared to the quantity of H_2S in the acid-gas stream.

Hydrogen cyanide is largely co-absorbed with the other acid gases and, if the absorbent solution does not contain oxidants, will end up with the acid-gas stream. In the direct-recovery processes HCN is converted to stable thiocyanates, which will build up in the solution and require that a portion of the solution be purged.

If condensible hydrocarbons are absorbed, poor-quality black sulfur will be produced by direct-recovery processes. Hydrocarbons in the acid-gas feed to the Claus unit will increase the combustion air required and necessitate that the Claus thermal oxidizer be operated at a higher temperature to assure complete combustion of hydrocarbons. If the hydrocarbons are only partly oxidized, the catalyst beds can become plugged or a poor-quality sulfur can result.

Generally the alkaline salt and alkanolamine processes will not appreciably absorb hydrocarbons. The physical-solvent processes, however, will readily absorb hydrocarbons heavier than butane.

D. CONDITION OF FEED GAS

Most processes are carried out at near-ambient temperatures (16 to 54°C). The physical-solvent processes are most effective at lower temperatures, and some require that the gas be chilled. In most of the currently applied alkaline salt processes elevated temperatures of up to 149°C can be used.

The physical-solvent processes and most alkaline salt processes require a high pressure, above 150 psig, to function efficiently. The alkanolamine and direct-recovery processes are generally independent of pressure and can be used equally well over a wide range of pressures.

E. CAPITAL AND OPERATING COSTS

The bottom line in choosing a process is the capital and operating costs. Generally the more sulfur contained in the gas the less the cost on a unit basis ($/tonne) to remove it. If sufficient sulfur compounds are present in the gas, an indirect-recovery process followed by a Claus sulfur recovery unit will provide the best economics. The physical-solvent processes are more economical when the acid-gas content is high or when the gas exists at high pressure. The alkaline

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salt processes have an advantage over other processes when the gas is at high pressure and high temperature and contains moderate amounts of acid gas. The alkanolamine processes are most economical when the gas is at low pressure and contains little CO_2. For gases that contain little H_2S or that have very high CO_2/H_2S ratios the direct-conversion processes may be more economical than the indirect-conversion processes. If complete removal of H_2S is required and the gas contains little H_2S, the solid-bed processes may be the most economical ones.

VI. DUTY REQUIREMENTS FOR OIL-SHALE RETORT-GAS-DESULFURIZATION SYSTEMS

A. CLASSIFICATION OF OIL-SHALE RETORTING PROCESSES

From the standpoint of removing sulfur compounds from oil-shale retort gases all retort processes can be divided into two broad and widely separated categories: those in which direct-fired retorts are used either above or below ground (in-situ), where combustion occurs within the retort; and those in which indirect-heated retorts are used and the shale is retorted in the absence of air.

The application of desulfurization technology for gases produced from direct-fired oil-shale retorting processes is distinctly different from that required for natural gas, coke-oven gas, refinery gas, or gas produced by coal gasification or, for that matter, for gas produced from indirect-heated oil-shale retorting process. Typical compositions of the gases are shown in Table 22.[1–3] The gas from direct-fired retorts contains large amounts of inert components, over 63% N_2 and 22% CO_2, but the H_2S content is less than 0.3%; it also contains large amounts of ammonia and unsaturated hydrocarbons, such as acetylene, ethylene, propylene, butylene, and butadiene. More than 40 hydrocarbon compounds have been identified in the gas; it is saturated with water and contains some oxygen and trace amounts of sulfur species other than H_2S.

Table 23 gives the range of gas compositions from direct-fired retorts, and Table 24 gives the range of those produced by indirect-heated retorts. The overiding factor that separates the two groups of processes and that will be dominant in selection of sulfur removal processes is the CO_2/H_2S ratio. For direct-fired retorts the CO_2/H_2S ratio ranges from 76:1 to more than 165:1, thus requiring a sulfur removal process that will selectively remove H_2S. Indirect-heated retorts produce a CO_2/H_2S ratio in the range of 4.3:1 to 5:1 which would allow a nonselective process to be used. As defined in Table 25 H_2S selectivity is the molar ratio of H_2S absorbed to CO_2 absorbed. If an indirect recovery process were to be used in conjunction with a

Table 22. Comparison of Fuel Gases

	Oil-Shale Gas		Coal Gasification				
Parameter	Direct-Fired Retort[a]	Indirect-Heated Retort	Lurgi[c]	Koppers-Totzek[c]	Coke Oven Gas[d]	Refinery Gas[c]	Natural Gas[e]
Components, vol %							
H_2S	0.3	4.1	1.1	1.6	0.3	62.5	2.6
CO_2	22.8	20.4	31.2	7.0	2.2	4.9	1.4
NH_3	0.7	8.3	0.2		1.0		
CH_4	2.1	20.2	9.4		27.2	8.4	82.3
C_2	1.2	16.0	0.7			5.2	5.2
C_3	0.7	10.5			4.0	4.6	1.8
C_4	0.6	5.2				10.0	1.0
C_5+	0.6		0.7			4.4	0.8
H_2	4.7	20.2	39.1	32.7	52.4		
N_2	63.8		0.6	1.2	4.1		4.8
O_2	0.1		0.6		0.1		
CO	2.5	3.4	17.3	57.4	8.5		
HCN			2.8		0.2		
Temperature, °C	60	60	454	1482	35	50	Amb
Pressure, psia	Atm	Atm	300	15	Atm	22	939

[a] See Table III-10.

[b] See Table III-19.

[c] See ref 1.

[d] See ref 2.

[e] See ref 3.

Table 23. Range of Gas Compositions from Direct-Fired Retorts[a]

Oil assay	62.5 to 125 ℓ/tonne
Gas ratio	224 to 405 sm^3/tonne
Composition (dry basis)	
Carbon dioxide (CO_2)	23 to 39 vol %
Hydrogen sulfide (H_2S)	0.07 to 0.24 vol %
Carbonyl sulfide (COS)	0 to 40 ppm
Ammonia (NH_3)[b]	0.6 to 0.7 vol %
Water (H_2O) (wet basis)	13.5 to 15 vol %
Gas mole ratio	
CO_2/H_2S	76:1 to 165:1[c]
NH_3/H_2S	2.3:1 to 2.4:1[d]
Temperature	57 to 77°C
Higher heating value (dry gas)	1.52×10^6 to 4.13×10^6 joules/sm^3

[a] Based on Paraho PON, Occidental Oil Shale (Oxy) retorts 7 and 8, and Geokinetics retort 18.

[b] Ratio for Geokinetics is 0.07:1.

[c] High ratio occurs at start of Oxy burn and averages about 330:1 during the startup phase. At steady-state conditions an average ratio of about 165:1 is obtained.

[d] Ratio reduces to 2.4:1 at steady state for the Oxy retort.

Table 24. Range of Gas Compositions from Indirect-Heated Retorts[a]

Oil assay	158 ℓ/tonne
Gas ratio	29.9 to 38.5 sm^3/tonne
Composition (dry basis)	
Carbon dioxide (CO_2)	16.6 to 20.4 vol %
Hydrogen sulfide (H_2S)	3.8 to 4.1 vol %
Carbonyl sulfide (COS)	135 to 550 ppm
Carbon disulfide (CS_2)	0 to 20 ppm
Alkyl mercaptans (RSH)	35 to 165 ppm
Sulfur dioxide (SO_2)	0 to 125 ppm
Ammonia (NH_3)[b]	8 vol %[c]
Water (H_2O) (wet basis)	20 to 25 vol %
Gas mole ratio	
CO_2/H_2S	4.3:1 to 5.0:1
NH_3/H_2S	2.1
Temperature	60 to 71.1 °C
Higher heating value (dry gas)	35.20×10^6 to 42.46 joules/sm^3

[a] Based on Tosco-II and Union SGR-3 retorts.

[b] Absorbed in sour water condensed with the oil.

[c] Calculated value.

Table 25. Selectivity Data

Selectivity =

$$\frac{(H_2S\text{ feed} - H_2S\text{ treated gas})/H_2S\text{ feed}}{(CO_2\text{ feed} - CO_2\text{ treated gas})/CO_2\text{ feed}} = \frac{H_2S\text{ Claus gas}/H_2S\text{ feed}}{CO_2\text{ Claus gas}/CO_2\text{ feed}} =$$

$$= \frac{CO_2\text{ feed}}{H_2S\text{ feed}} \times \frac{H_2S\text{ Claus gas}}{CO_2\text{ Claus gas}} = \frac{\text{mole \% } H_2S\text{ absorbed}}{\text{mole \% } CO_2\text{ absorbed}}$$

For direct-fired retorts $\frac{CO_2\text{ feed}}{H_2S\text{ feed}} = \frac{76}{1}$ to $\frac{165}{1}$

For indirect-fired retorts $\frac{CO_2\text{ feed}}{H_2S\text{ feed}} = \frac{5}{1}$

For Claus feed gas $\frac{H_2S}{CO_2} > 0.08$ to 0.25

Selectivity required

Direct-fired retorts = $\frac{76}{1} \times (0.08 \text{ to } 0.25) = 6 \text{ to } 19$

= $\frac{165}{1} \times (0.08 \text{ to } 0.25) = 13 \text{ to } 41$

Indirect-fired retorts = $\frac{5}{1} \times (0.08 \text{ to } 0.25) = 0.4 \text{ to } 1.25$

Claus sulfur recovery process, the acid-gas feed to the Claus unit should be as rich in H_2S as possible and consist of at least 8 to 25% H_2S. Gases from direct-fired retorts with CO_2/H_2S ratios in the range of 100:1 to 200:1 would require H_2S selectivity in the range of 8 to 50 to produce an acceptable Claus gas (see Table 25); however, gas from indirect-fired retorts would produce an acceptable Claus gas only if all the CO_2 were removed along with the H_2S.

The quantity of H_2S and NH_3 in the gas per ton of shale processed is, as shown in Table 26 about equal for both direct- and indirect-retorting processes. The quantity of sulfur contained in an equal volume of gas, on the other hand, is as much as 60 times greater for indirect-fired retorts than for direct-fired retorts. Thus a gas treatment system for a direct-fired retort would have to process up to 60 times more gas per ton of sulfur recovered than would a system processing gas from indirect-heated retorts.

B. COMMERCIAL OIL-SHALE OPERATIONS

The projected sizes of several commercial oil-shale processing facilities are given in Table 27. All full-scale processing facilities will consist of multiple retort systems with several trains of gas treating equipment.

The data given in Tables 22 and 23 are based on the gas discharged from the retort after the oil is separated. The actual composition and condition of the gas as it reaches the sulfur removal train may be somewhat different for a full-scale commercial plant if additional product recovery and gas treating steps are incorporated. For most direct-fired-retort processes water scrubbing will be used to remove ammonia from the gas and to cool the gas before it enters the sulfur removal equipment. Some developers propose to compress and then cool the gas to recover additional hydrocarbons. Some may elect to upgrade the raw crude by coking and hydrotreating and/or direct hydrogenation. Residual gases from these operations would likely be added to the feed to the sulfur removal units.

Table 26. Comparison of Gas Treatment Duty Requirements

	Direct-Fired Retorts	Indirect-Heated Retorts
Duty Range Per 45,450 Tonnes of Shale Processed		
Gas rate (Msm^{3}D)	10.2--18.4	1.4--1.8
Hydrogen sulfide (tonnes)	33.6--64.5	78.2--85.4
Other sulfur compounds (tonnes)	0.04--2.0	0.6--3.3
Carbon dioxide (tonnes)	4,545--32,087	443--545
Ammonia (tonnes)	38--95	83--106
Total sulfur (tonnes)	32--62	74--83
Duty Range Per Million Cubic Feet of Gas Treated		
Shale processed (tonnes)	70--126	734-947
Hydrogen sulfide (kg)	30--103	1,636--1,773
Other sulfur compounds (kg)	.5--3	12--64
Carbon dioxide (kg)	12,727--21,818	9,250--11,363
Ammonia (kg)	130--151	1,727--1,818
Total sulfur (kg)	29--99	1,547--1,710

Table 27. Commercial Oil-Shale Operations

		Near-Term Development Capacity					Projected Full-Scale Operation				
Company	Type of Process	No. of Retorts Operating	Shale Processed (tonnes/ day)	Crude Oil Produced (m^3/day)	Raw Gas Produced (M sm^3d)	Sulfur in Gas (tonnes/ day)	No. of Retorts Operating	Shale Processed (tonnes/ day)	Crude Oil Produced (m^3/day)	Raw Gas Produced (M sm^3d)	Sulfur in Gas (tonnes/ day)
Geokinetics[a]	Direct	1			.06	0.09	16	5,454	320	2.8	
Paraho[b]	Direct	1	10,000	960	2.23	9	24	143,094	15,867	32.1	120
Occidental[c]	Direct	2	5,363	336	1.58	5.5	40	149,076	9,120	48.3	131
Tosco II [d]	Indirect	6	60,000	8,800	2.32	174.5	6	60,000	8,800	2.3	175
Union[e]	Indirect	1	9,090	1,440	0.27	14.5	6	47,886	8,000	1.4	120

[a] See refs 4 and 5.

[b] See refs 5, 6 and 7.

[c] See refs 7 and 8.

[d] See refs 7 and 9.

[e] See refs 10 and 11.

Indirect-retort gases that have high heating values may be combined with residual gases from other process steps and may undergo several treatment steps before they reach the sulfur removal equipment. For instance the shale-oil hydrocarbon vapors from the pyrolysis drum of the proposed Colony Tosco-II facility will be separated in a fractionator into sour water, gas, naphtha, gas oil, and bottom oil. The gas and naphtha are piped to a gas recovery and treating unit. The other streams are further treated to upgrade the product. The residual gases from product upgrading units are combined with the gas stream from the fractionator and then compressed and fed to the gas recovery and treating unit along with raw naphtha recovered from various treatment units. Stabilized naphtha, LPG, butanes, butadiene/butylenes, and ammonia are separated and recovered. The remaining gas then enters the sulfur removal equipment. Acid gas with residual ammonia from the sour-water stripper and from the ammonia separation unit is sent directly to the Claus sulfur recovery unit.

For the purpose of this report it is assumed that the composition of the gas is as discharged from the retort after the oil has been separated.

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VII. SCREENING OF GAS TREATING PROCESSES

Gases from direct-fired retorts are more limiting in the application of sulfur-removal technology than are other gases (see Sect. VI-A). In the course of this study it was determined by the EPA that the greatest immediate concern was the control of sulfur emissions from direct-fired processes and that the pilot-plant design should be applicable to these retorting methods. Therefore process selection was directed toward the requirements for desulfurization of gas from direct-fired retorts.

As is indicated in Table 23, treating gas from direct-fired retorts requires a process with high selectivity toward H_2S. The initial screening of principal commercial gas-conditioning processes was therefore based on the ability of each process to selectively remove H_2S in the presence of large amounts of CO_2. Those processes most capable of selectively removing H_2S were selected as candidates for more detailed evaluations. The processes referred to are shown on Fig. 9, a duplicate of Fig. 6. For the purpose of the initial screening, selectivities near the midpoint of the selectivity range reported in the literature were used (see Table 28).

A. DIRECT-CONVERSION PROCESSES

In the direct-conversion processes the sulfur compounds are directly oxidized to elemental sulfur or are converted to another compound, which is then separated or recovered.

1. Dry Bed

Several dry-bed direct-conversion processes have been tested but none are known to have been commercially applied. These processes are similar to the Claus process except that the SO_2 necessary for the reaction is obtained by burning sulfur in an external burner and the gas to be treated is preheated to the operating temperature of the catalyst beds. To maintain high conversion efficiency the catalyst beds are regenerated more frequently than is required by the Claus process. One version is designed so that the catalyst is continually

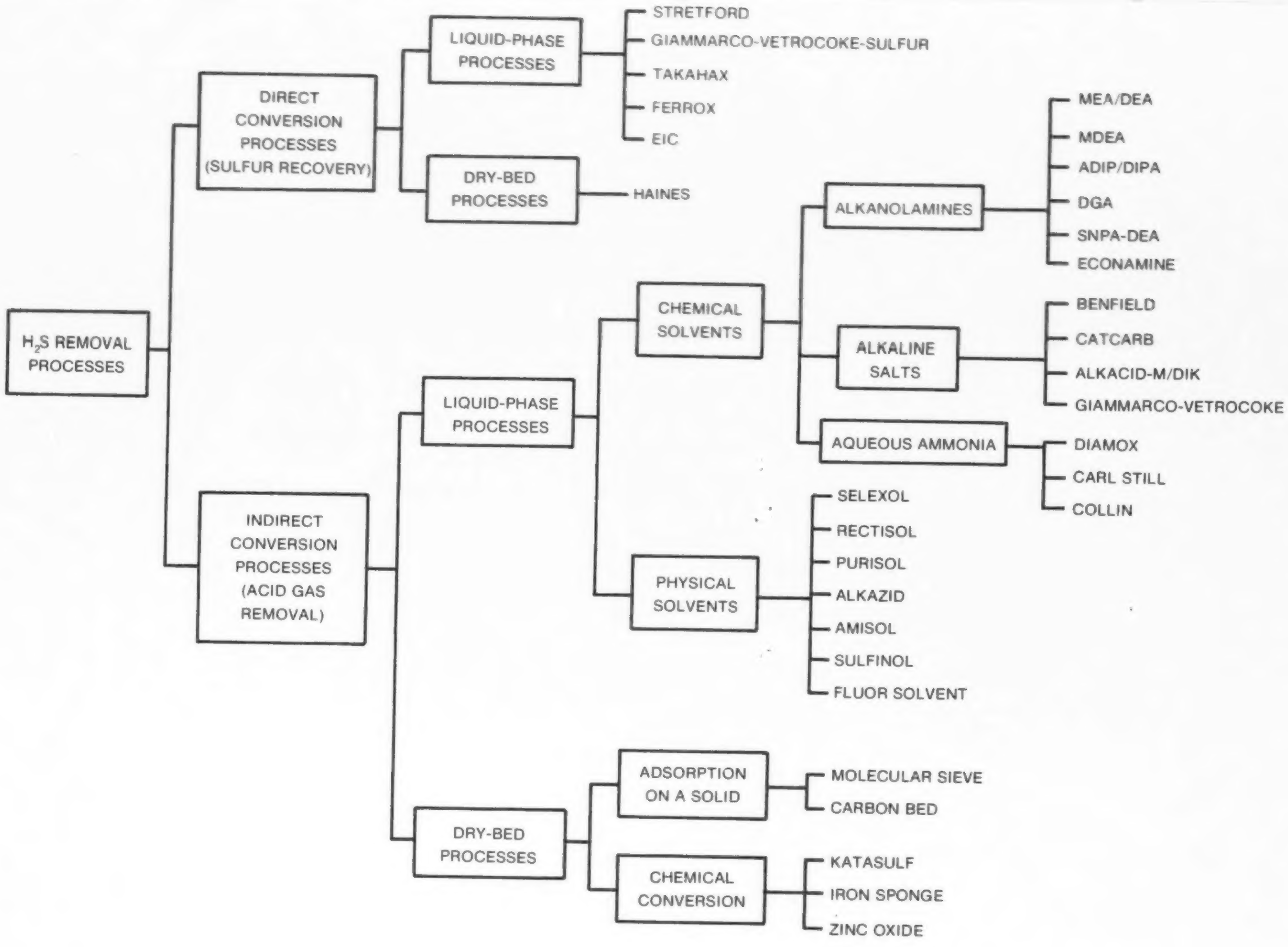

H$_2$S REMOVAL PROCESSES
DIRECT CONVERSION PROCESSES (SULFUR RECOVERY)
LIQUID-PHASE PROCESSES
STRETFORD
GIAMMARCO-VETROCOKE-SULFUR
TAKAHAX
FERROX
EIC
DRY-BED PROCESSES
HAINES
INDIRECT CONVERSION PROCESSES (ACID GAS REMOVAL)
LIQUID-PHASE PROCESSES
CHEMICAL SOLVENTS
ALKANOLAMINES
MEA/DEA
MDEA
ADIP/DIPA
DGA
SNPA-DEA
ECONAMINE
ALKALINE SALTS
BENFIELD
CATCARB
ALKACID-M/DIK
GIAMMARCO-VETROCOKE
AQUEOUS AMMONIA
DIAMOX
CARL STILL
COLLIN
PHYSICAL SOLVENTS
SELEXOL
RECTISOL
PURISOL
ALKAZID
AMISOL
SULFINOL
FLUOR SOLVENT
DRY-BED PROCESSES
ADSORPTION ON A SOLID
MOLECULAR SIEVE
CARBON BED
CHEMICAL CONVERSION
KATASULF
IRON SPONGE
ZINC OXIDE

Figure 9. Gas-Sweetening Processes

Table 28. Selectivity of Absorbent Processes

Absorbent	Selectivity Range	Reported By
MEA	0.89	Pearce[a]
DEA	1.2 to 2.27	Pearce[a]
MDEA	1.2 to 7.0	Pearce[a]
DIPA	3.33 to 5	Naber *et al.*[b]
NH_3	1.00 to 28.9	Kohl and Riesenfeld[c]
Diamox	5.7 to 9.4	Hiraoka *et al.*[d]
Benfield	2.25 to 9.8	Parrish and Neilson[c]
Selexol	5 to 22	Kohl and Riesenfeld[f]

[a] See ref 5.

[b] See ref 6.

[c] See ref 10.

[d] See ref 13.

[e] See ref 9.

[f] See ref 14.

withdrawn from the bottom of the bed and the regenerated catalyst is added at the top.[1]

The Haines process uses a bed of synthetic zeolite to adsorb the H_2S. The bed is then regenerated with high-temperature gas that contains sulfur dioxide. The sulfur formed is condensed and recovered.

The application of these processes is limited due to the possibility that the beds will be plugged by condensible hydrocarbons and/or other impurities in the gas. Since these processes have not been commercially proven, they are not considered further.

2. Liquid Phase

Except for the EIC process the principal liquid-phase direct-conversion processes shown on Fig. 9 selectively remove H_2S by converting it directly to elemental sulfur. Carbon dioxide is only slightly absorbed and largely remains in the treated gas. With the EIC process, sulfur is removed as ammonium sulfate and CO_2 is not removed.

The Stretford, Giammarco-Vetracoke (G-V), and Takahax processes are based on similar oxidation-reduction chemistry but use different activator chemicals. The G-V process uses an arsenic compound, but because of arsenic's toxicity the process is not applied in this country. The Takahax process, developed in Japan, has not been widely applied.

The Ferrox process, which is based on the reaction between iron oxide and H_2S, is outdated and has been replaced by the more efficient Stretford Process. In the Stretford process, the direct-conversion process most often employed, H_2S is selectively removed by direct oxidation to elemental sulfur but CO_2 is only slightly absorbed. The process is usually the preferred choice when the H_2S concentration in the raw gas is very low or when a high degree of selectivity is required. Complete removal of H_2S to about 1 ppm can be obtained in the treated gas. Since the sulfur absorption capacity of the Stretford solution is low, the process is not competitive with indirect sulfur removal processes for volumes of H_2S in the feed gas that exceed about 16% of the total acid-gas content of the gas.[2]

Organic sulfur compounds are not removed by the Stretford process but remain in the treated gas. Stable thiosulfates form in the oxidizer equivalent to about 1% of the sulfur in the feed gas. A portion of the circulating solution must be purged to control the buildup of these compounds. The quality of sulfur produced is low compared to that produced by the indirect-recovery processes. In spite of its shortcomings the Stretford process has been widely applied, and when the CO_2/H_2S ratio is very high, it may be the only process available that is capable of economically purifying the gas.

The EIC process is an absorption-oxidation process using copper sulfate as the absorbent that produces by-product ammonium sulfate from the hydrogen sulfide and ammonia in the treated gas. The process reportedly removes H_2S and COS and ammonia but does not remove CO_2.[3] A high removal efficiency of 99% is obtained in one absorption step and the system can operate at elevated temperature. The process is in the development stage and has not been commercially proven. However, since it appears to match the requirements needed for desulfurization of direct-fired oil-shale gases, it will be considered as a canidate for further evaluation.

B. INDIRECT-CONVERSION PROCESSES

In the indirect conversion processes the acid-gas components are removed from the fired gas and recovered as a separated stream that is subsequently processed for recovery of sulfur.

1. Dry Bed

The dry-bed indirect-conversion processes provide excellent selectivity, with most of them capable of removing sulfur compounds with little or no CO_2 removal. These processes use a fixed bed of solid material. Processes that use molecular sieves or carbon adsorb the sulfur compounds, which are subsequently released unchanged during regeneration of the bed. With the iron sponge and zinc oxide processes, H_2S reacts with the bed to form iron or zinc sulfide. The Katasulf process is based on the catalytic oxidation of H_2S to SO_2, followed by removal of SO_2 with an ammonium sulfite—bisulfite solution.

Dry-bed processes, however, are limited in their application and become economically impractical for those cases where large amounts of gas have to be treated or the total quantity of sulfur to be removed is high. Since full-scale oil-shale facilities will be processing huge amounts of gas beyond the practical limit for application of dry-bed processes, these processes are not considered further.

2. Liquid Phase

With liquid-phase indirect-conversion processes the acid-gas components are removed from the feed gas by absorption into liquid. The liquid is subsequently regenerated to produce a concentrated stream of acid gas, which is then processed by the Claus process for recovery of the sulfur. The principal liquid-phase indirect-conversion processes are shown on Fig. VII-1 and are classified by type.

a. Alkanolamines—The alkanolamine processes are based on the reaction of a weak base (alkanolamine) and a weak acid (H_2S, organic acids, and/or CO_2) to form a water-soluble salt:

$$RNH_2 + H_2S \longrightarrow RNH_3^+ \cdot HS^-$$

$$RNH_2 + CO_2 + H_2O \longrightarrow RNH_3^+ \cdot HCO_3^-$$

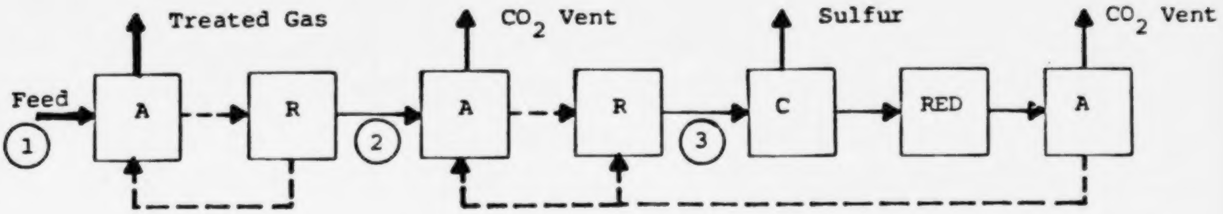
These reactions are reversible, and the equilibrium may be shifted by adjustment of the solution temperature. The absorption of CO_2 involves the formation of carbamates as intermediate compounds. With primary and secondary amines the carbamates are formed nearly instantly and the reaction rate of CO_2 with the amine is nearly equal to that of H_2S with amine. With tertiary amines carbanates form at a much slower rate and therefore H_2S is absorbed more readly than is CO_2. This difference in reaction rates between H_2S and CO_2 accounts for the higher selectivities that are obtained with tertiary amines. Methyldiethanolamine (MDEA) reportedly produces the highest selectivity of the tertiary amines[4—6] (see Table 28).

The selectivity at which H_2S can be absorbed in the presence of CO_2 depends on absorption kinetics rather than on equilibrium effects. The actual selectivity obtained by a process is dependent on several variables, the most readily controlled being the absorber contact time. In practice high selectivity is obtained by limiting the number of contact stages in the absorber and the residence time per stage. Absorption kinetics are also affected by a variety of other process variables, including competition between H_2S and CO_2 when they are absorbed simultaneously. The degree of H_2S removal decreases as the contact time is reduced in an attempt to increase the selectivity. The extent of selectivity that can be obtained will be restricted by the purity required of the treated gas. To reasonably predict these effects for a specific gas composition and at a specified degree of desulfurization, the process developers have devised proprietary computer programs for modeling the absorption process.[7,8] These models were developed and verified through extensive laboratory and field testing programs.

The average selectivity of MDEA as reported by Pearce[5] is 3.85. If a two-stage selective absorption system were used and a selectivity of 3.85 per stage were obtained, the H_2S in the acid-gas stream would be about 12.9 vol % for a feed gas with a CO_2/H_2S ratio of 100:1 (see Table 29). If the ratio were 200:1, the acid gas would contain about 6.9% H_2S, which is marginally acceptable. A possible process option would be a system consisting of two or more stages of selective absorption, with MDEA used as the solvent.

b. Alkaline Salts——The principal alkaline salt processes, shown on Fig. VII-1, are most successfully applied for bulk CO_2 removal but are not generally considered when selective absorption of H_2S is required.

Table 29. Selective Absorption Using MDEA with Two Stages of Absorption


Treated Gas
CO_2 Vent
Sulfur
CO_2 Vent
Feed
①
A
R
②
A
R
③
C
RED
A

A = absorption; R = regeneration; C = Claus; RED = reduction.

Stream	CO_2/H_2S Ratio[a]	H_2S (vol %)[b]
Case 1		
① Feed 1st stage	100	1.0
② Feed 2nd stage	26	3.7
③ Claus gas	6.7	12.9
Case 2		
① Feed 1st stage	200	0.5
② Feed 2nd stage	51.9	1.9
③ Claus gas	13.5	6.9
Case 3		
① Feed 1st stage	4	20.0
② Feed 2nd stage	1.04	49.0
③ Claus gas	0.27	78.7

[a] Based on obtaining selectivity ratio of 3.85 per stage.

[b] As vol % of total CO_2 and H_2S.

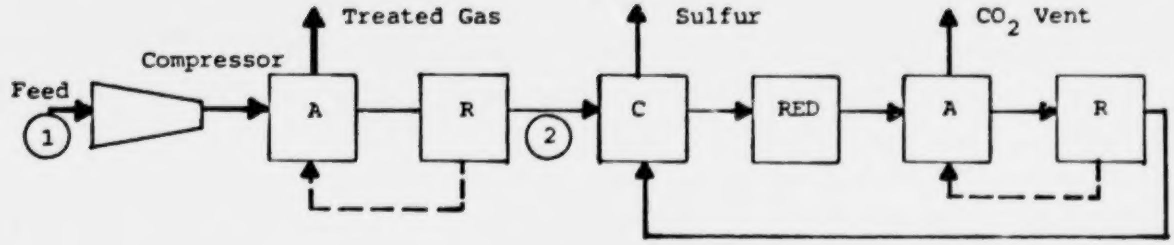
The Catacarb process is not highly selective in H_2S removal and the Giammarco-Vetrocoke process, designed for bulk CO_2 removal, uses an arsenic compound to improve the solution reactivity. The Alkacid process using DIK solvent will selectively absorb H_2S. However, the capacity of the solution for absorbing H_2S and the degree of H_2S removal obtained decrease as the the CO_2/H_2S ratio of the feed gas increases.

The Benfield process is normally applied for bulk removal of acid gas. A high degree of H_2S removal can be obtained when the CO_2/H_2S ratio is high and both acid gases are simultanelusly absorbed. However, the acid-gas stream produced is usually too lean for Claus processing. Since H_2S is absorbed more rapidly than CO_2 in a potassium carbonate solution, the process can be made to selectively absorb H_2S; but, as the selectivity increases, the degree of removal of H_2S decreases.

The Benfield HiPure process, a two-stage process using an amine solution in the second stage to absorb residual H_2S and optimized to take advantage of the higher solubility and absorption rate of H_2S, has produced selectivities of up to 9.8 based on data reported by Parrish and Neilson.[9] If an average selectivity of 6 were obtained with the Benfield HiPure process (see Table 30), the H_2S content of the acid gas would be approximately 5.7 for a feed gas with a CO_2/H_2O ratio of 100:1 or 2.9 if the ratio were 200:1. In either case insufficient selectivity would be obtained to provide an acceptable Claus gas.

To apply the Benfield process, the feed gas must be at high pressure, above 100 psig. The higher the pressure, the more efficient the process and the higher the selectivity that is obtained. Since gas from proposed oil-shale retorts would be produced at near-atmosphere pressure, the gas would have to be compressed. The capital and operating costs of compressing the gas cannot be justified by use of the Benfield process. Also, since H_2S is less soluble in the alkaline salt solution at higher temperatures, the advantage that hot gases can be fed to the process is offset somewhat in that selectivity decreases as the temperature increases.

Table 30. Selective Absorption by Benfield Process


Treated Gas
Sulfur
CO_2 Vent
Compressor
Feed
1
A
R
2
C
RED
A
R

A = absorption; R = regeneration; C = Claus, RED = reduction.

Stream	CO_2/H_2S Ratio[a]	H_2S (vol %)[b]
Case 1		
① Feed	100	1.0
② Claus gas	17	5.7
Case 2		
① Feed	200	0.5
② Claus gas	33	2.9
Case 3		
① Feed	4	20.0
② Claus gas	0.7	60.0

[a] Based on selectivity ratio of 6.

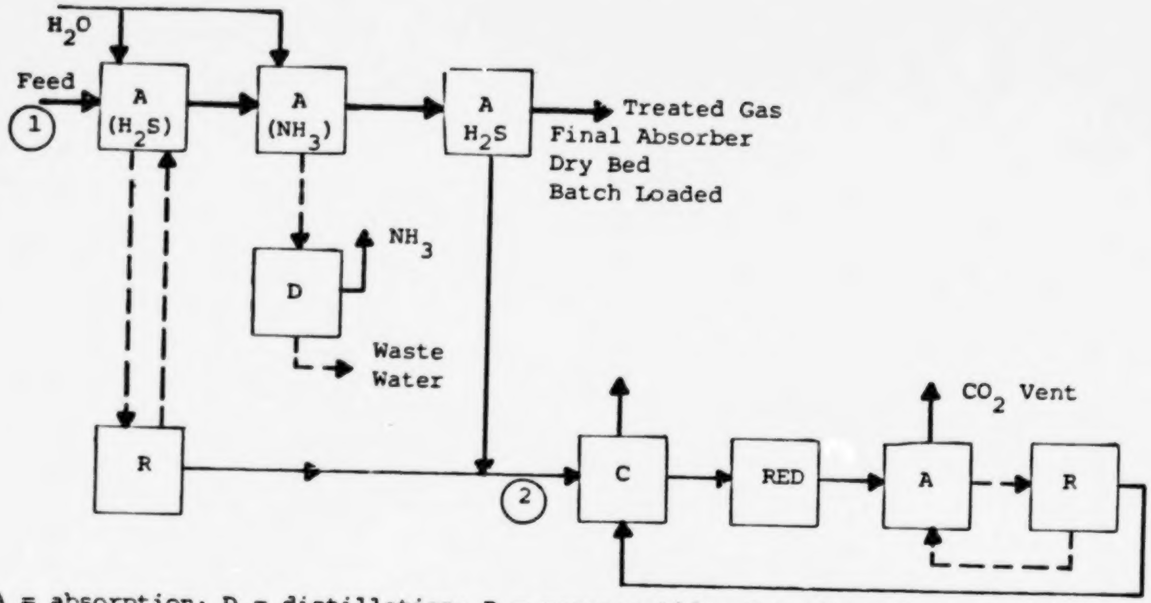
[b] As vol % of total CO_2 and H_2S.

c. Aqueous Ammonia Processes——Aqueous ammonia processes have been used since the end of the nineteenth century for removal of hydrogen sulfide and nitrogen compounds, primarily ammonia from coal gas. Many ammonia-based processes have been developed over the years; the principal ones used today are shown on Fig. 9. Ammonia-based processes are particularly applicable to gases containing both H_2S and ammonia. The ammonia contained in the gas can serve as the active agent for removal of H_2S and can be recovered as a by-product.

If the physical parameters of the absorption process are controlled, aqueous ammonia solution can selectively remove H_2S from gases containing CO_2. Selectivities of up to 28.9 have been reported.[10] Hydrogen sulfide ionizes immediately on contact with the solution and reacts rapidly with the hydroxyl ions, whereas carbon dioxide must first react with water, forming carbonic acid, before it can react ionically with ammonia. The rate of the CO_2 hydration reaction is quite low compared to the reaction rate of H_2S.[11]

The absorption of ammonia into water is quite rapid and is governed principally by the gas-film resistance. The rate of absorption of H_2S into aqueous ammonia solutions is also rapid although it is dependent on the ammonia concentration and is probably also governed by the gas-film resistance. Carbon dioxide absorption into water or weak alkaline solutions, on the other hand, is governed by its liquid-film resistance, which is very much greater than that for H_2S. As a result when gases containing H_2S, ammonia, and CO^2 are contacted with water or ammonia solution, the ammonia and H_2S are absorbed much more rapidly than is CO_2. This difference can be accentuated by operating under conditions that reduce the gas-film resistance or increase the liquid-film resistance. Thus to achieve maximum selectivity, spray columns in combination with relatively short contact times are used.[11] Table 31 shows the results that could be obtained if a selectivity of 28.9 were achieved. However, the degree of H_2S removal decreases as the selectivity is increased. Removal of about 90% of the H_2S is the maximum efficiency that can be attained economically through selective ab-

Table 31. Selective Absorption Using Aqueous Ammonia


H_2O
Feed
①
A
(H_2S)
A
(NH_3)
A
H_2S
Treated Gas
Final Absorber
Dry Bed
Batch Loaded
NH_3
D
Waste
Water
R
②
C
RED
A
R
CO_2 Vent

A = absorption; D = distillation; R = regeneration; C = Claus; RED = reduction.

Stream	CO_2H_2S Ratio[a]	H_2S (Vol %)[b]
Case 1		
① Feed	100	1
② Claus gas	3.46	22.4
Case 2		
① Feed	200	0.5
② Claus gas	6.92	12.6
Case 3		
① Feed	4	20.0
② Claus gas	0.14	87.8

[a] Based on selectivity ratio of 28.9.

[b] As vol % of total CO_2 and H_2S.

sorption. A final purification step must be added to remove the residual H_2S if it is desired to achieve a high degree of removal with a high degree of selective absorption.

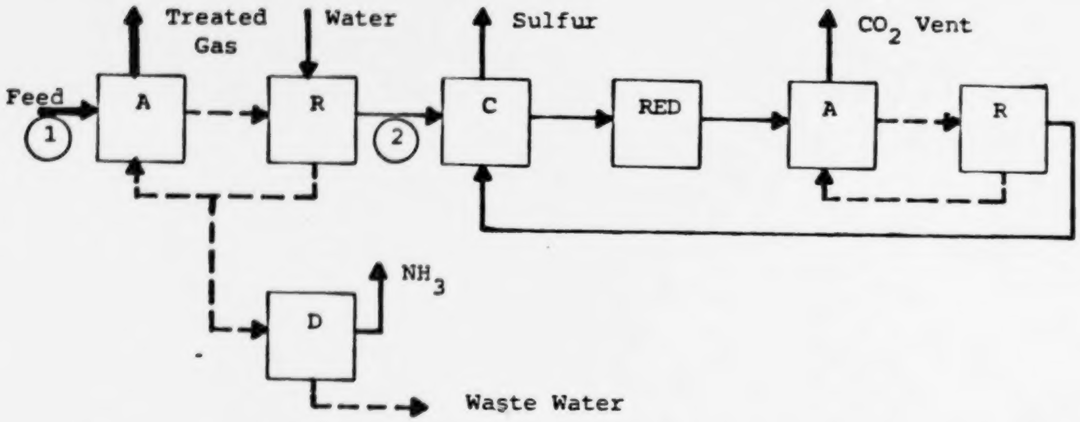
The selectivity of aqueous ammonia solutions decreases markedly at temperatures above 27°C.[12] Also, the selectivity decreases as the ammonia concentration of the solution is increased. However, the degree of H_2S removal increases as excess available ammonia is increased. The Diamox process, recently developed in Japan, was designed to take maximum advantage of these factors. Hydrogen sulfide removal in the range of 97 to 99%, with good selectivity still maintained, can be achieved by the Diamox process. Selectivities in the order of 5.7 to 9.4 have been obtained based on data reported by Hiraoka, Tanaka, and Sudo.[13] If an average selectivity of 7.6 were obtained with the Diamox process (Table 32), an acid gas containing 7.1% would be obtained for a feed gas with a CO_2/H_2S ratio of 100:1, or 3.7% H_2S would be obtained if the ratio were 200:1. The Diamox process would be marginally acceptable for gases with CO_2/H_2S ratios of up to about 100:1 but would not produce sufficient selectivity for direct-fired retort gases with higher CO_2/H_2S ratios.

d. Physical-Solvent Processes——Selectivity of physical-solvent processes depends on the relative solubilities of CO_2 and H_2S in the solvent. The capacity of the solution for absorbing H_2S increases with increasing pressure and decreasing temperature; generally the higher the partial pressure of H_2S the higher the selectivity attainable will be. Selectivity can also be enhanced by favorable absorber kinetics.

The Selexol process appears to produce the highest reported selectivity of the physical-solvent processes; H_2S is 9 times more soluble in the Selexol solvent than CO_2 is. Selectivity ratios of up to 22 have been obtained based on data reported by Kohl and Riesenfeld.[14]

To apply the Selexol process the retort gas would have to be compressed and cooled before it entered the absorber. If an average selectivity

Table 32. Selective Absorption by Diamox Process


Treated Gas
Water
Sulfur
CO_2 Vent
Feed
①
A
R
②
C
RED
A
R
D
NH_3
Waste Water

A = adsorption; D = distillation; R = regeneration; C = Claus; R = reduction.

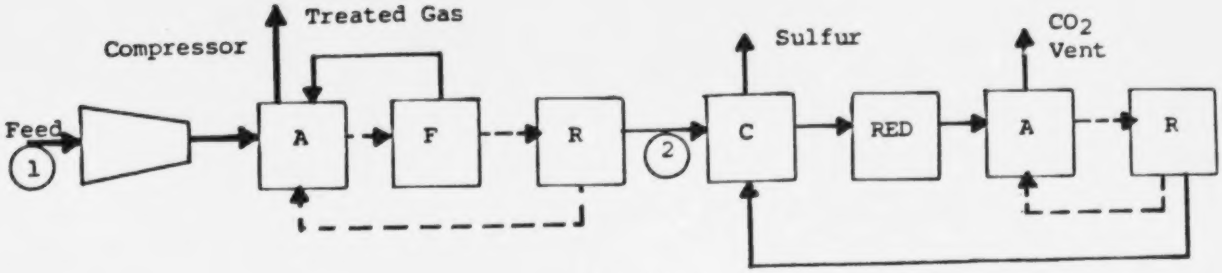
Stream	CO_2/H_2S Ratio[a]	H_2S (vol %)[b]
Case 1		
① Feed	100	1.0
② Claus gas	13.2	7.1
Case 2		
① Feed	200	0.5
② Claus gas	26.3	3.7
Case 3		
① Feed	4	20.0
② Claus gas	0.53	65.5

[a] Based on selectivity ratio of 7.6.

[b] As vol % of total CO_2 and H_2S.

of 13.5 were obtained as shown in Table 33 the acid-gas stream produced would range between 11.9 and 6.3% H_2S for a feed gas with CO_2/H_2S ratios in the range of 100:1 to 200:1.

Table 33. Selective Absorption by Selexol Process


Compressor
Treated Gas
Sulfur
CO_2 Vent
Feed
①
A
F
R
②
C
RED
A
R

A - absorption; F = flash; R = regeneration; C = Claus; RED = reduction.

Stream	CO_2/H_2S Ratio[a]	H_2S (vol %)[b]
Case 1		
① Feed	100	1.0
② Claus gas	7.4	11.9
Case 2		
① Feed	200	0.5
② Claus gas	14.8	6.3
Case 3		
① Feed	4	20.0
② Claus gas	0.30	77.1

[a] Based on selectivity ratio of 13.5.

[b] As vol % of total CO_2 and H_2S.

C. REFERENCES*

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2. S. Vasan, "Holmes-Stretford Process Offers Economic H_2S Removal," The Oil and Gas Journal 76(1), 78—80 (Jan. 2, 1978).

3. Letter dated Apr. 1, 1980, from W. Dyer, EIC Corporation, to R. Lovell, IT Enviroscience.

4. A. L. Kohl and F. C. Riesenfeld, op. cit., p 38.

5. R. L. Pearce, "Hydrogen Sulfide Removal with Miethyl Diethanolamine," pp 139—144, in Proceedings of the 57th Annual Convention of the Gas Processors Association, March 20—22, 1978, New Orleans.

6. J. Naber, J. Wesselingh, and W. Groenendaal, "New Shell Process Treats Claus Off-Gas," Chemical Engineering Progress 69(12), 29—34 (Decembe 1973).

7. C. Ouwerkerk, "Design for Selective H_2S Absorption," Hydrocarbon Processing 57(4), 89—94 (April 1978).

8. Telephone conversation Jan. 28, 1980, between C. A. Peterson, IT Enviroscience, and R. L. Pearce, Dow Chemical USA.

9. R. W. Parrish and H. B. Neilson, Synthesis Gas Purification Including Removal of Trace Contaminants by the Benfield Process, presented at the 167th National Meeting of the American Chemical Society, Division of Industrial and Engineering Chemistry, Los Angeles, California, March 31 to April 5, 1974.

10. A. L. Kohl and F. C. Riesenfeld, op. cit., p 148.

11. Ibid., p 134.

12. Ibid., p 151.

13. H. Hiraoka, Mitsubishi Chemical Industries, Ltd., and E. Tanaka and H. Sudo, Mitsubishi Kakoki Kaisha, Ltd., "DIAMOX Process for the Removal of H_2S in Coke Oven Gas," Proceedings of the Symposium on Treatment of Coke-Oven Gas, May 1977, McMaster University Press, Hamilton, Ontario, Canada.

14. A. L. Kohl and F. C. Riesenfeld, op. cit., pp 784—789.

*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

VIII. EVALUATION OF CANDIDATE PROCESSES

As determined from the data given in Sect. VII the processes that produce the highest H_2S selectivity or appear to be most applicable to treatment of gases from direct-fired oil-shale retorts are the following:

Direct-Conversion Processes

Stretford
EIC

Indirect-Conversion Processes

Alkanolamine processes——MDEA
Alkanline salt processes——Benfield
Aqueous ammonia processes——Diamox
Physical solvent processes——Selexol

A. BASIS OF EVALUATION

To furthur evaluate these processes their capabilities were compared, with a hypothetical feed gas composition used as the basis for comparison. The gas composition chosen (Table 34) is similar to the gas produced by the Paraho direct-fired retort. Trace organic sulfur compounds, not included in Paraho's data, were added so that their effects could be evaluated. The quantity of trace sulfur compounds shown was extrapolated from data compiled from sources reporting on trace compounds.[1]

The indirect sulfur removal processes are only marginally capable of producing an acceptable Claus gas when the CO_2/H_2S ratio of the feed gas exceeds about 100:1 (see Tables 29 through 33). The hypothetical gas, with a CO_2/H_2S ratio of 73:1, was chosen so that it would be within the capabilities of the more marginal processes. To treat this gas, using an indirect removal process, an H_2S selectivity ratio of at least 6 would be required to produce a minimally acceptable acid gas for the Claus unit.

Table 34. Hypothetical Direct-Fired Retort Gas

Physical Properties	Product Gas Composition (wet basis)	Amount (wet vol %)
Retort off-gas temperature: 66°C		
Retort off-gas pressure: 20 psia		
Gas rate: 224 sm^3/tonne of shale		
Gas density: 1.2 kg/m^3		
Molecular weight: 28.43		
	H_2	3.539
	O_2	0.743
	N_2 + Ar	51.342
	CO	1.600
	CO_2	17.572
	CH_4	1.858
	C_2H_4	0.743
	C_2H_6	0.768
	C_3H_6	0.364
	C_3H_8	0.380
	C_4S (MW = 57.0)	0.323
	C_5S (MW = 71.5)	0.129
	C_6 + (MW = 96.2)	0.622
	H_2S	0.242
	NH_3	0.566
	H_2O	19.210
		100.000[a]

[a] Includes the following trace compounds: COS, 36 ppm; CS_2, 7 ppm; RSH, 10 ppm; and SO_2, nil.

Projected plans for full-scale commercial oil-shale plants based on direct-fired retort technology range from Geokinetics' facility producing 2.83 million m^3 of gas per day from 16 retorts processing about 5454 tonnes of shale per day[2] to Occidental's MIS plant producing 48 million m^3 of gas per day from a series of 40 retorts processing about 149,078 tonnes of shale per day.[3]

The model plant selected for evaluation of a sulfur removal process has a capacity of 45,450 tonnes of shale per day and produces 10.2 million m^3 of gas a day based on the composition of the hypothetical gas. A desulfurization plant in this size range will require multiple trains to process the volume of gas produced, as would be the case for most projected commercial oil-shale facilities. The individual components required for the model-plant sulfur removal train should therefore be in the size range of that required for a full-scale commercial oil-shale facility and should be representative of such a facility.

B. GAS PRETREATMENT

Most sulfur removal processes will require some form of pretreatment of the gas before it enters the sulfur removal equipment. For most processes the gas must be cooled and ammonia, condensible hydrocarbons, and excess water be removed. Other processes may require compression of the gas. Particulate matter is largely removed in the oil separation and gas cooling steps. Additional particulate removal is not required before the gas enters desulfurization equipment.

1. Gas Cooling and Ammonia Removal

The temperature of raw gases produced by direct-fired oil-shale retorts range from 57° to 77°C. For most sulfur removal processes the gas must be cooled before it enters the absorber. Since the gases from direct-fired retorts are saturated with water, large amounts of water will be condensed out as the gas is cooled. Calculations indicate that sufficient water can be condensed to simultaneously absorb and remove the ammonia contained in the gas if the gas is cooled to about 32°C.

The gas cooling unit for the model plant is shown in Fig. VIII-1. The raw fuel gas (stream 1), which is at 60°C, is directly contacted with the cooling water in a packed tower to bring the temperature down to 32°C. As the gas cools, a large portion of the water vapor, 849 kg/min, and a small amount of hydrocarbons are condensed into the circulating cooling water. Essentially all the ammonia, a stoichiometric amount of CO_2, and a small amount of H_2S are absorbed into the cooling water. The cooled gas (stream 3) is sent to the desulfurization system absorber.

A portion of the cooling water solution equilivent to the quantity of gases and vapors absorbed is purged (stream 2) from the system. The remaining cooling water solution, saturated with CO_2, is passed through a heat exchanger to remove the heat absorbed and then recirculated. The operating conditions and the composition of the recirculating cooling water are controlled so that minimum H_2S is absorbed into the cooling water.

The purge stream will be treated (not shown) by being passed through an oil separator, where condensed hydrocarbons are recovered, and then through a sour-water stripper and ammonia recovery unit. The H_2S recovered in the sour-water stripper is returned to the process gas stream. The ammonia is stripped and recovered as a by-product. The remaining water, which contains trace amounts of absorbed organics, H_2S, and ammonia, is sent to a conventional wastewater treatment system.

2. Condensible Hydrocarbons

The heavier hydrocarbons with boiling points above 90°F will condense and be largely removed in the gas cooling unit. However, components in the gas include unsaturated hydrocarbons such as acetylene, ethylene, propylene, butadiene, and butylene. These components will not condense as the gas is cooled. They can, however, polymerize and form tarry substances that can foul the acid-gas absorber, discolor the sulfur, or clog the catalyst beds of a Claus sulfur recovery unit if polymeriza-

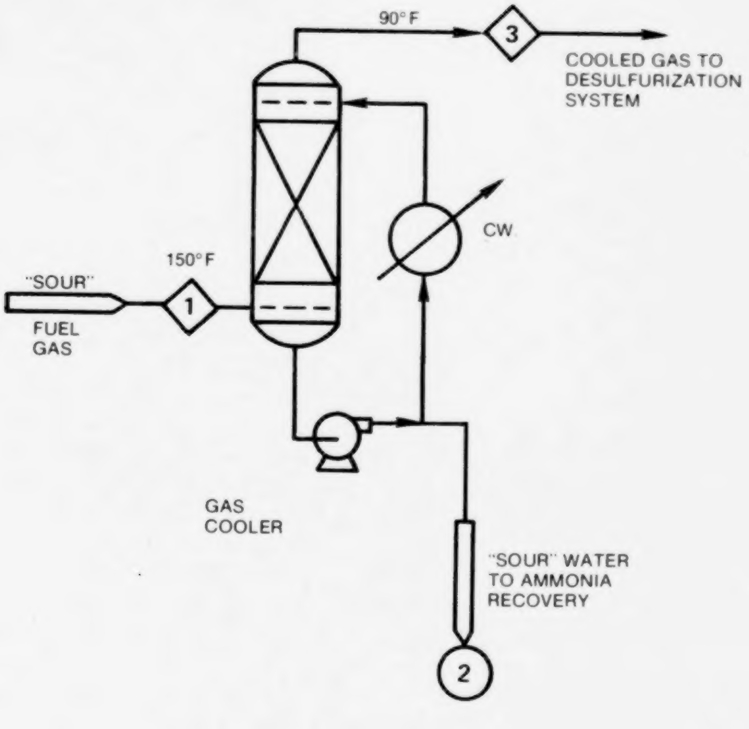
90° F
3
COOLED GAS TO DESULFURIZATION SYSTEM
CW
150° F
"SOUR"
1
FUEL GAS
GAS COOLER
"SOUR" WATER TO AMMONIA RECOVERY
2

Figure 10. Gas Cooler/Ammonia Absorption System

tion takes place in the acid-gas absorber. There is no economical way of removing these compounds before the gas enters the acid-gas absorber, and their effects on the desulfurization train can be determined only by testing of the process.

3. Gas Compression

Both the Benfield and the Selexol processes require elevated pressure to operate and thus would require gas compression. For the model plant producing 10.2 million sm^3d of gas (Table 34) a compressor rated at 84,500 hp would be required to boast this pressure to 150 psig. A gas-turbine-driven compressor system of this capacity with intercoolers and condensate separation is estimated to cost $6 to $8 million and would consume about $34,500 of fuel per day, or about 32% of the treated gas produced by the facility.

If the treated gas were combusted in a gas turbine used for power generation, a portion of the available energy in the compressed gas would be recovered as the gas expanded through the turbine. Thus if the gas is compressed, it would be advantageous to remove as little CO_2 as possible in the desulfurization process so that more gas will be available to expand through the turbine. However, after compression the gas would have to be cooled to the operating temperature of the sulfur removal process, and so a large portion of the available energy in the form of heat would be removed before the compressed gas reached the power generation turbine. From an energy standpoint it would be more efficient to compress the gas as it enters the power generation turbine rather than before sulfur removal.

Since the Benfield process can operate at up to 121°C, less heat would have to be removed from the compressed gas than with the Selexol or other processes that operate below 32°C. Approximately 4673.6×10^9 joules of heat per day would have to be extracted to cool the compressed gas to 121°C, at a cost of about $1750/day for cooling water. To cool the compressed gas to 32°C approximately $10,118 \times 10^9$ joules/day must be extracted at a cost of $3850/day.

Compressing the gas to 150 psig would reduce its volume by a factor of 6 to 10, depending on the exit temperature. Thus the number or size of absorbers required to handle the gas would be reduced porportionately for those processes in which the absorber size is gas limiting (Selexol, Benfield, and to some extent the alkanolamine processes). For those processes in which the absorber size is liquid limiting (Stretford, Diamox, and to some extent MDEA) the size of the absorbers may not be significantly different if the gas were compressed.

Due to the high capital and operating costs of gas compression it is not economical to compress the gas for the purpose of sulfur removal alone. Some full-scale commercial oil-shale plants employing indirect-heated retorts may compress the gas before sulfur removal for the purpose of recovering LPG and other condensible hydrocarbons or for other process reasons. In that case the application of the Benfield or Selexol process may be attractive.

C. DIRECT-RECOVERY PROCESSES

1. The Stretford Process (See Appendix A)

The Stretford process was developed in England jointly by the North Western Gas Board and the Clayton Aniline Company, Ltd.[4] The process has been proven commercially over a period of many years in more than 80 plants built around the world.[5] Several modifications and improvements to the basic process have been made by various companies that now license their proprietary versions of the Stretford process. The principal licensors in this country are Peabody Process Systems of Stamford, Connecticut, the Pritchard Corporation of Kansas City, Missouri, and the Ralph M. Parsons Company of Pasadena, California.

The chemistry of the Stretford process is relatively complex. The idealized reactions illustrate the absorption, oxidation/reduction cycle as follows:[6]

Reaction 1

$$Na_2CO_3 + H_2S \longrightarrow NaHS + NaHCO_3$$

Reaction 2

$$4NaVO_3 + 2NaHS + H_2O \longrightarrow Na_2V_4O_9 + 2S + 4NaOH$$

Reaction 3

$$Na_2V_4O_9 + 2NaOH + H_2O + 2ADA \longrightarrow 4NaVO_3 + 2ADA \text{ (reduced)}$$

Reaction 4

$$2ADA \text{ (reduced)} + O_2 \longrightarrow 2ADA + H_2O$$

A flow diagram of the Stretford process for fuel gas desulfurization is shown in Fig. 11. The sour fuel gas (stream 1) enters the gas cooler, where it is cooled and a large portion of the water and most of the ammonia are removed (stream 2) and sent to foul water treatment. The cooled gas (stream 3) enters the Stretford absorber at about 32°C. The feed gas (stream 3) is countercurrently washed with an aqueous solution containing sodium carbonate, sodium metavanadate, and anthroquinone disulfonic acid (ADA). The H_2S rapidly dissolves and ionizes in the alkaline solution, forming a small amount of sodium hydrosulfide (reaction 1). Hydrosulfide loadings in the solution range from 500 to 1000 ppm; thus relative large amounts of solution must be circulated. The sodium metavanadate in the solution readily reacts with the hydrosulfide to produce elemental sulfur (reaction 2).

Sodium carbonate in the solution provides a pH buffer to prevent rapid pH changes as the acid gases are absorbed. The alkalinity of the Stretford solution causes some of the CO_2 to be absorbed along with the H_2S. The treated gas (stream 4) with essentially all the H_2S removed exits from the top of the absorber. The aqueous solution enters the delay tank, with sufficient residence time provided to assure that any

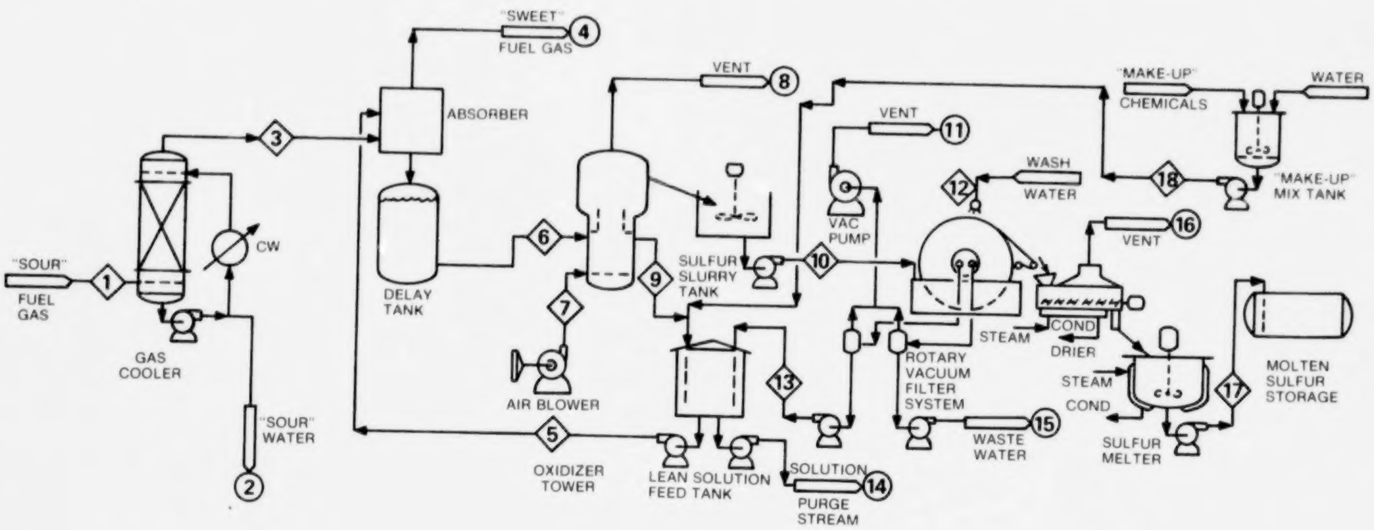
"SOUR"
FUEL GAS
1
GAS COOLER
CW
"SOUR" WATER
2
3
ABSORBER
"SWEET" FUEL GAS
4
DELAY TANK
6
7
AIR BLOWER
5
OXIDIZER TOWER
VENT
8
9
SULFUR SLURRY TANK
LEAN SOLUTION FEED TANK
SOLUTION PURGE STREAM
14
13
10
VENT
11
VAC PUMP
WASH WATER
12
ROTARY VACUUM FILTER SYSTEM
WASTE WATER
15
STEAM
COND
DRIER
VENT
16
STEAM
COND
SULFUR MELTER
17
MOLTEN SULFUR STORAGE
"MAKE-UP" CHEMICALS
WATER
"MAKE-UP" MIX TANK
18

Figure 11. Stretford Process for Fuel-Gas Sulfurization

remaining hydrosulfide is reacted so as to prevent hydrosulfide from entering the oxidizer and becoming oxidized to stable sodium thiosulfate, an undesirable by-product. Thiosulfate can be formed by oxygen dissolved in the Stretford solution, oxygen in the feed gas, or hydrosulfide carryover to the oxidizer. An excess of vanadate is maintained to avoid overloading the solution with hydrosulfide. Formation of thiosulfate can be controlled somewhat by controlling the pH and the temperature of the solution. Thiosulfate can be allowed to concentrate in the solution to about 20% by weight. A small portion of the solution (stream 14) is then continually purged and replaced to prevent further accumulation and crystallization of salts.

The reduced solution (stream 6) is regenerated in the oxidizer tower by being sparged with an excess of air. The reduced vanadium is reoxidized to its original state through oxygen transfer via the ADA (reaction 3). The reduced ADA is reoxidized by contact with air (reaction 4). Reoxidation of the ADA can be appreciably accelerated by the presence of small amounts of iron salts kept in solution by a chelating agent, ethylenediamine tetracetic acid (EDTA).[7]

The nitrogen and the excess oxygen from the air bubble upward through the solution, floating sulfur particles to the top as a froth and stripping the dissolved gases. The froth, which contains about 10% solids, overflows the oxidizer to a slurry tank. A damp cake containing 50 to 60% solids is produced by filtration or centrifugation of the slurry (stream 10). The sulfur cake can be further processed by washing to remove the Stretford chemicals and by drying and melting to produce liquid or solid sulfur (stream 17).

The regenerated solution (stream 5) is relatively free of sulfur and is pumped back to the absorber. In route the solution must normally be cooled to maintain the desired operating temperature, which is usually accomplished in an evaporative cooling tower. To maintain water balance in the system due to the addition of sulfur and/or filter wash water and water produced by the reaction, water is evaporated with the treated gas or in the cooling tower. A solution heater is sometimes required for winter operation or to assure sufficient evaporation.

Carbon dioxide is partly absorbed by the alkaline solution, resulting in the formation of sodium bicarbonate and consequent lowering of pH. The solution eventually reaches equilibrium with respect to the concentration of CO_2 in the gas stream, after which only relatively small amounts of CO_2 are absorbed. Since the vanadate-ADA system functions at a lower pH, decarbonation of the solution is not required. When the gas contains high concentrations of CO_2, the absorption efficiency of the solution may be lowered to the extent that an appreciable increase in absorber height will probably be required. Peabody has developed a proprietary venturi-absorber that is insensitive to the H_2S/CO_2 ratio and is capable of handling fuel gas containing 85% CO_2 with minimum absorption of CO_2.[8]

The principal side reactions that are detrimental to the process are the formation of thiosulfates and thiocyanates. If hydrosulfate is contacted with oxygen before it is converted to sulfur, thiosulfate will form, the amount depending on the pH of the solution and on the operating temperature. The rate of thiosulfate formation under favorable conditions can be held to less than 1 wt % of the sulfur in the feed gas by controlling the pH and temperature of the solution and by assuring that sufficient delay time has occurred for the conversion of H_2S to sulfur before the solution reaches the oxidizer tower. However, gases from direct-fired retorts contain oxygen and a large amount of CO_2. Calculations show that for those gases about 3 to 4% of sulfur in the gas will go to thiosulfate as the result of oxygen in the feed gas and the buffering action of the CO_2. Fortunately, oil-shale gases contain only trace amounts of hydrogen cyanide (HCN). Hydrogen cyanide will react with elemental sulfur to form stable thiocyanide, which also accumulates in the solution.

For small plants producing less than about 9 tonnes of sulfur per day, the wet sulfur cake is often disposed of by approved methods in a landfill. Since the wet cake contains sufficient thiosulfate, additional purge of the solution is not required to control thiosulfate buildup. For plants producing more than 9 tonnes per day it may be more economical to recover the sulfur, in which case a small stream of solution must be continually purged.

As thiosulfate is purged from the system it carries with it a proportionate amount of Stretford chemicals, which must be replaced (stream 18). It is important therefore to permit thiosulfate to concentrate in the solution to as high a level as the process will allow (20 to 22%) to minimize the costs of replacement chemicals and waste disposal.

The purge stream containing toxic vanadium salts with an average COD (chemical oxygen demand) of 20,000 mg/liter can be difficult to treat and dispose of. Treatment methods used include evaporation or spray drying, biological degradation, oxidative combustion, and reductive incineration. Peabody Holms has successfully developed a zero-discharge reductive incineration process that cracks the bleed liquor into a gas stream containing H_2S and CO_2, along with a liquid stream containing reduced vanadium salts that can be returned to the system.[8] The problem of disposing of wastewater containing vanadium is eliminated and no makeup of vanadium or sodium salts is required. However, makeup water to the system must be demineralized and the feed gas to the Stretford absorber must be free of soluble minerals to prevent inorganic solids from building up in the system.

The Stretford process is insensitive to pressure and can operate in the range of atmospheric to maximum pipeline pressure. Operating temperatures range from ambient to 49°C . Any type of gas-liquid contacting device may be used as an absorber. Problems of plugging have been encountered in packed towers, especially with gases containing high concentrations of H_2S (above 1%).[9] Therefore large rings or saddles are recommended when packed towers are used. Venturi scrubbers have been successfully used for gases containing larger amounts of H_2S, up to 15%.[10]

Stretford plants are remarkably free of corrosion tendencies and can be constructed entirely of carbon steel, with inert linings, e.g., cold-cured epoxy resins, used for oxidizers and sulfur froth tanks. Stainless steel linings are recommended for solution and sulfur slurry pumps.[11]

The Stretford process is extremely flexible in operation and can tolerate wide variations in both gas feed rate and H_2S concentration in the feed gas. Startup and shutdown are relatively simple and can be accomplished in short periods of time. Good process control is maintained by simple analytical testing with little technical supervision. Since all process streams are handled as liquids, the process is easily automated and requires little operator attention.[5]

Hydrogen sulfide removal to less than 10 ppmv can be obtained with normal operation of a Stretford plant. Assuming that the gas contains COS in the range of 10 to 50 ppmv the overall sulfur removable achievable by the Stretford process would be in the range of 98.0 to 99.3%.

2. The EIC Process

The EIC process was developed by EIC Corporation of Newton, Massachusetts, for removal of H_2S from geothermal steam. The process has been field tested in a pilot plant processing 45,454 kg of steam per hour at The Geysers in California.[12] Although the process has not yet been pilot tested on desulfurization of fuel gases, EIC is promoting the process for that purpose.

Geothermal steam contains noncondensable gases such as carbon dioxide, hydrogen sulfide, ammonia, methane, nitrogen, hydrogen, traces of radon, argon, and mercury vapor, as well as rock dust, boron compounds, and other particulates.[12] In The Geysers test desulfurization to about 11 ppm H_2S in the exhaust steam was achieved.[12]

The EIC process is an absorption oxidation process using copper sulfate as the absorbent, which produces ammonium sulfate from hydrogen sulfide and ammonia in the treated gas. From the geothermal tests and from laboratory analysis EIC has found that the process has the following advantages: the process removes H_2S and COS but does not remove CO_2; high removal efficiency of 99% is obtained in one absorption step; the systems can operate at elevated temperatures in the range of 66 to 260°C; ammonia in the gas is removed and ends up in the by-product ammonium sulfate produced by the process; and the capital and operating costs are reasonable.[13]

The chemistry of the EIC copper sulfate process is summarized as follows:[14]

Scrubbing

H_2S Removal: $H_2S + CuSO_4 \longrightarrow CuS + H_2SO_4$

NH_2 Removal: $2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

Regeneration

$CuS + 2O_2 \longrightarrow CuSO_4$

Net Result

$H_2S + 2NH_3 + 2O_2 \longrightarrow (NH_4)_2SO_4$

A flow diagram for the process is shown in Fig. 12. The raw gas at 66°C (stream 1) is scrubbed with a sulfuric acid solution of copper sulfate, which precipitates the hydroden sulfide as an insoluble copper sulfide and removes the ammonia by forming soluble ammonium sulfate. The precipitated copper sulfides (stream 2) are separated from the purge stream in a continuous decanter and are converted back to copper sulfate (stream 3) by leaching with oxygen. The purge stream (4) is neutralized with ammonia. The neutralized stream (5) is then treated intermittently with iron and hydrogen to remove any soluble copper for recycle to the process. The resulting effluent (stream 6), which is

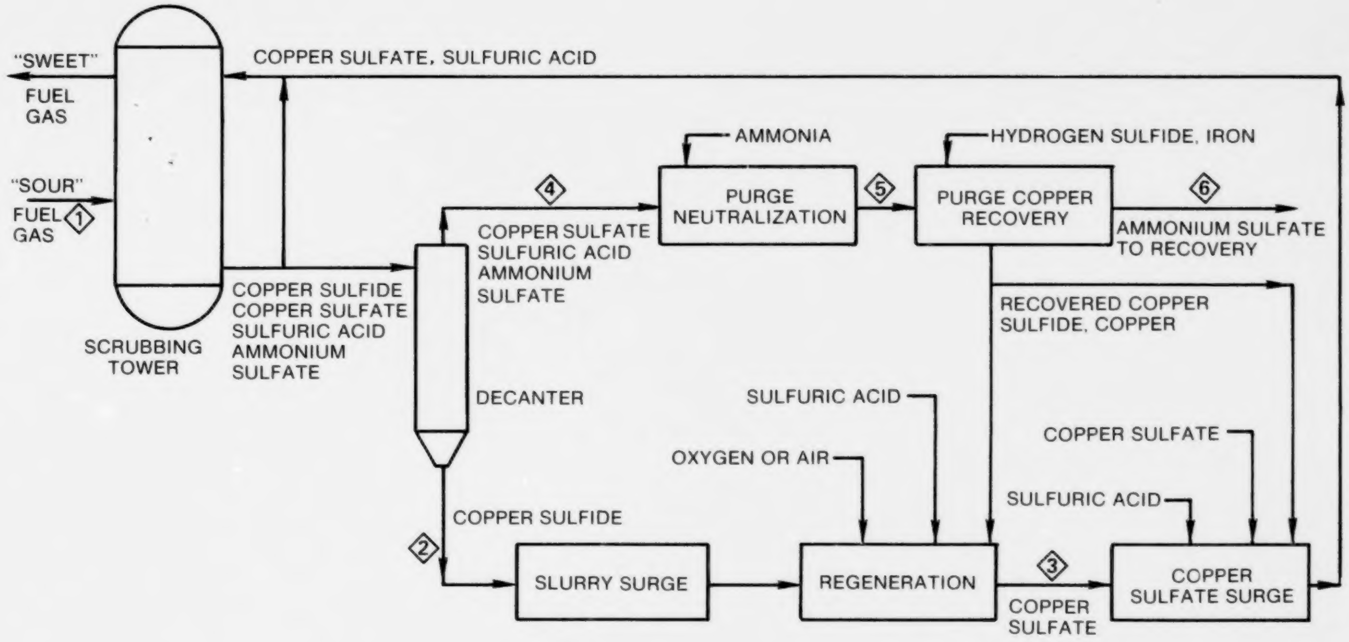
"SWEET" FUEL GAS
"SOUR" FUEL GAS
1
SCRUBBING TOWER
COPPER SULFATE, SULFURIC ACID
COPPER SULFIDE COPPER SULFATE SULFURIC ACID AMMONIUM SULFATE
DECANTER
4
COPPER SULFATE SULFURIC ACID AMMONIUM SULFATE
AMMONIA
PURGE NEUTRALIZATION
5
HYDROGEN SULFIDE, IRON
PURGE COPPER RECOVERY
6
AMMONIUM SULFATE TO RECOVERY
RECOVERED COPPER SULFIDE, COPPER
SULFURIC ACID
OXYGEN OR AIR
COPPER SULFATE
SULFURIC ACID
COPPER SULFIDE
2
SLURRY SURGE
REGENERATION
3
COPPER SULFATE
COPPER SULFATE SURGE

Figure 12. EIC Sulfuric Acid—Copper Sulfate Process

primarily ammonium sulfate, can be recovered by removing the water in a vacuum crystallizer.[13]

Extensive use of titanium is required in the construction of the system because of the corrosiveness of the sulfuric acid—copper sulfate solution.[14] The size of the components, however, is much smaller than that of components for competing processes as the result of irreversible reactions occurring in the absorber and of the reactiveness and concentration of the solution. The smaller size of the equipment offsets a large part of the cost involved in the use of special materials of construction. EIC believes that the capital and operating costs of the system, including ammonium sulfate recovery equipment, are competitive with those of the Stretford process.[12]

The process appears to be well suited to desulfurization of oil-shale gas since it removes both H_2S and COS, as well as ammonia, and would not require that the feed gas be cooled. However, there are many unanswered questions, and more development work needs to be done before the process is applied to oil-shale gas. A potential major problem is that oil-shale gas contains various unsaturated hydrocarbons, which could react with the strong sulfuric acid—copper sulfate solution and form undesirable by-products. Of particular concern is the large amount of acetylene in the gas. If the highly unstable compound cuprous acetylide were to form and accumulate in the system, it could become very hazardous. Cuprous acetylide is explosive and can be detonated by percussion or can explode when heated above 100°C. If warmed in air or oxygen for several hours, it will explode when brought in contact with acetylene.[15] The potential for formation of cuprous acetylide in the EIC copper sulfate solution has not, to our knowledge, been defined.

Another potential problem could be entrainment of the solution in the treated gas. Carryover could cause corrosion of the downstream piping and gas turbine blades. The process has not been sufficiently proved to recommend its use at this time. The process could become a viable candidate for desulfurization of oil-shale gases if through testing and development the adverse effects of corrosion and undesirable side reactions are proved not to create a problem.

D. INDIRECT-RECOVERY PROCESSES

Table 35 gives the approximate volume and H_2S concentration of the acid-gas stream that the model plant would produce for each of the indirect-recovery-process options. The selectivity data used for this table are either the average selectivity data reported in the literature[16—18] for the process or, as in the case for the MDEA[19] and the Diamox[20] processes, are the actual selectivity calculated for the process based on the gas composition assumed for the model plant. For the purpose of this comparison it was assumed that all H_2S and a portion of the CO_2 relative to the average selectivity obtained by the process would be removed and end up in the acid-gas stream to the Claus unit.

Based on the requirements of a minimum acceptable volume of about 8% of H_2S in the acid-gas feed to the Claus unit and of the need for at least 25% H_2S for effective operation, the table indicates that a one-stage selective absorption process using DEA or MDEA would not produce a sufficient level of H_2S in the acid-gas stream for operation of the Claus sulfur recovery process. Two stages of selective absorption using MDEA as the absorbent would be marginal, as would one stage of selective absorption using either the Diamox, the Benfield, or the Selexol process. Three stages of selective absorption using MDEA, however, would produce an acid gas rich enough in H_2S for economic operation of the Claus unit.

It can be noted that the volume of acid gas produced decreases as the selectivity of the process increases. Thus when high selectivity is achieved, the volume of gas that must be processed by the succeeding absorption stage or by the Claus unit is considerably reduced, thereby reducing the equipment size and its installation and operating costs.

Table 35. Comparison of Selective Absorption Processes for Treating Gas from a Direct-Fired Retort[a]

			Acid-Gas Stream to Claus Unit				
Absorbent	Number of Stages	Selectivity	CO_2 (sm^3d)	H_2S (sm^3d)	Total (sm^3d)	Total (sm^3d)	H_2S (dry vol %)
DEA	1	2[b]	895,129	24,649	919,778	640	2.7
MDEA	1	2.4[c]	745,812	24,649	770,467	535	3.2
MDEA	2	8.2[c]	219,466	24,649	244,172	170	10.1
MDEA	3	27.4[c]	65,316	24,649	89,994	62	27.4
Diamox	1	4.7[d]	379,531	24,649	404,181	280	6.1
Benfield	1	6[e]	299,782	24,649	323,016	224	7.6
Selexol	1	9[f]	198,921	24,649	280,170	156	11.0

[a] Conditions:
Gas rate = 45,450 tonnes/day X 224 sm^3/tonne = 10,188,000 sm^3d; CO_2 = 17.572 vol % = 1,782,900 sm^3d; H_2S = 0.247 vol % = 24,649 sm^3d.

[b] See ref 16.

[c] See ref 19.

[d] See ref 20.

[e] See ref 17.

[f] See ref 18.

The Benfield and Selexol processes, while only marginally capable of producing an acid gas of acceptable concentration, require high pressure to operate. The high cost of gas compression caused these processes to be categorically eliminated from further considerations (see discussion in Sect. VIII-B3).

The indirect-process candidates therefore were narrowed to a three-stage alkanolamine (MEDA) process and the Diamox process. A third candidate that was evaluated is a one-stage selective system coupled with a Stretford unit for recovery of sulfur from the acid gas. A discussion of these systems follows.

1. Three-Stage Selective Absorption Using MDEA as the Absorbent (See Appendix B).

Two principal commercial processes are available based on the use of amine solutions for selective absorption of H_2S in the presence of CO_2: the Selectamine process developed by Dow Chemical USA at Freeport, Texas, and the Adip process developed by Shell International Petroleum Company, The Hague, The Netherlands. The Adip process uses the secondary amine diisopropanolamine (DIPA) or the tertiary amine methyldiethanolamine (MDEA). The Selectamine process uses MDEA as the absorbent.

The basic flow steps for all alkanolamine acid-gas absorption systems are similar. As shown in Fig. 13, the gas to be purified (stream 3) enters the bottom of the absorber and passes upward countercurrent to the aqueous MDEA solution. The lean solution reacts with and chemically absorbs the H_2S and a portion of the CO_2 as it contacts the gas in the absorber. The purified gas (stream 4) exits at the top of the absorber and the rich solution containing the absorbed acid gas (stream 6) is drawn off at the bottom. To achieve the highest practical selectivity, absorption kinetics are carefully controlled through absorber design and operation (see discussion in Sect. VII-B2a). The selectivities achieved and the approximate volumes of gas handled by each stage are given in Table 35.

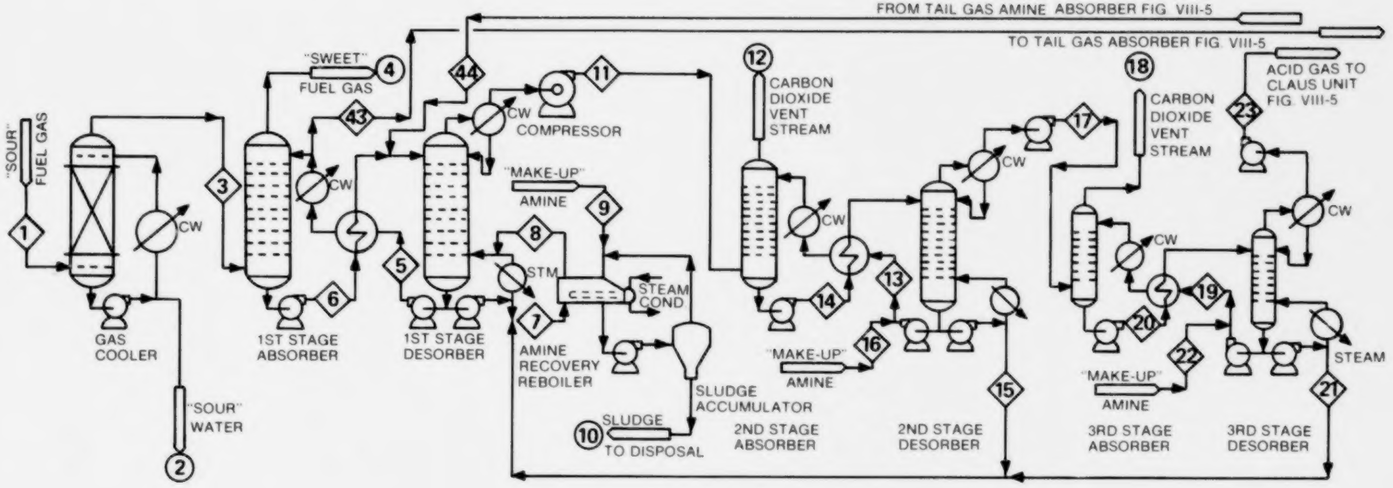
FROM TAIL GAS AMINE ABSORBER FIG. VIII-5
TO TAIL GAS ABSORBER FIG. VIII-5
"SOUR" FUEL GAS
1
GAS COOLER
CW
"SOUR" WATER
2
3
1ST STAGE ABSORBER
"SWEET" FUEL GAS
4
43
CW
6
5
44
1ST STAGE DESORBER
CW
COMPRESSOR
11
"MAKE-UP" AMINE
9
8
STM
7
AMINE RECOVERY REBOILER
STEAM COND
SLUDGE ACCUMULATOR
10
SLUDGE TO DISPOSAL
12
CARBON DIOXIDE VENT STREAM
CW
14
13
"MAKE-UP" AMINE
16
2ND STAGE ABSORBER
CW
2ND STAGE DESORBER
15
17
18
CARBON DIOXIDE VENT STREAM
CW
20
19
"MAKE-UP" AMINE
22
3RD STAGE ABSORBER
23
ACID GAS TO CLAUS UNIT FIG. VIII-5
CW
STEAM
21
3RD STAGE DESORBER

Figure 13. Three-Stage MDEA Selective Absorption System

The sulfur removal effectiveness usually decreases as measures are taken to increase the selectivity. For the process described the H_2S content of the treated gas can be reduced to about 10 ppmv and the COS will be reduced by about 60%. The total sulfur reduction of the treated gas, assumed to contain 10 to 50 ppmv COS, would be in the range of 99.2 to 99.5%.

The rich solution (stream 6) is heated by heat exchange with the hot lean solution from the bottom (stream 5) of the stripping column and then enters the stripping column near the top. The lean solution partially cooled in the heat exchanger is further cooled by exchange with water and then fed into the top of the absorber.

In the stripper the absorption reactions are reversed as the temperature of the solution is increased. The desorbed acid gas exiting at the top of the stripping column is cooled to condense out the water vapor as the acid gas (stream 11) continues on to the next absorption stage. The condensed water is fed back at the top of the stripper above the point of the rich-solution entry. This serves to absorb the amine vapors carried out by the acid-gas stream.

The reaction between MDEA and organic sulfur compounds is not readily reversed. A side stream (7) of lean solution is sent to a reclaimer, where a portion of the degraded solution is recovered by high-temperature distillation. The bottoms (stream 10) accumulated from the reclaimer are sent to waste disposal.

The acid gas produced by the first-stage system (535 sm^3/m) becomes the feed for the next absorption stage. Compared to the gas entering the first-stage absorber (see Table 36) the quantity of gas that must be treated by the second-stage absorber has been reduced by 92% and the CO_2/H_2S ratio reduced to 30.8.

The second-stage absorber operates nearly identically to the first-stage absorber. The treated gas (stream 12), however, is high-purity

Table 36. Performance of Three-Stage Selective Absorption System Using MDEA

Stage	Feed Gas Volume (sm^3m)	Acid-Gas Stream Volume (sm^3m)	Volume Reduction[a] (%)	H_2S (%)	CO_2 (%)	CO_2/H_2S Ratio[b]	CO_2/H_2S % Reduction[c]
1	7,075	535	92.4	3.2	96.8	30.8	57.6
2	535	170	97.6	10.1	89.9	8.9	87.7
3	170	62	99.1	27.4	72.6	2.6	96.4

[a] Volume reduction related to volume of feed gas to first-stage absorber.

[b] CO_2/H_2S ratio of feed gas to first-stage absorber is 72.6.

[c] CO_2/H_2S ratio reduction related to feed gas entering first-stage absorber.

CO_2, which contains about 10 ppmv H_2S and is often used as a by-product when a local market exists for it.

The acid gas (170 sm^{3}m) (stream 17) produced by the second-stage system contains about 89.9% CO_2 and 10.1% H_2 and has a CO_2:H_2S ratio of about 8.9.

The third-stage absorber also produces high-purity CO_2 (stream 18). The acid gas (62 sm^{3}m) (stream 23), containing about 73% CO_2 and 27% H_2S with a CO_2:H_2S ratio of about 2.6, is rich enough in H_2S content to be processed by a modified Claus system for sulfur recovery.

In the operation of the Claus unit (described in Sect. IV-B) the sulfur burning— by-pass process is used since it is the least costly option and since the acid gas produced by the three-stage selective absorption process is free of hydrocarbon contamination (see Fig. 14).

The SCOT tail-gas treatment was chosen because it can be integrated with the selective absorption system to save total installation costs. Since both systems use MDEA as the absorbent, the regeneration of the rich solution coming from the SCOT unit can be combined with regeneration of the absorbent from the primary absorber.

The SCOT process consists essentially of two parts: a reduction stage in which all sulfur compounds and elemental sulfur in the off-gas are reduced to H_2S and an absorption stage in which, after water is removed by condensation, H_2S is selectively removed by MDEA absorption/regeneration and is recycled to the Claus unit. The total sulfur recovery of the Claus unit can be increased to above 99.8% of the sulfur in the acid-gas feed. The SCOT unit is flexible, having a wide operating range, and no secondary waste streams are produced.[21]

The estimated overall sulfur reduction calculated for the total desulfurization train is about 98.8 to 99.3%, depending on the quantity of organic sulfur in the gas.

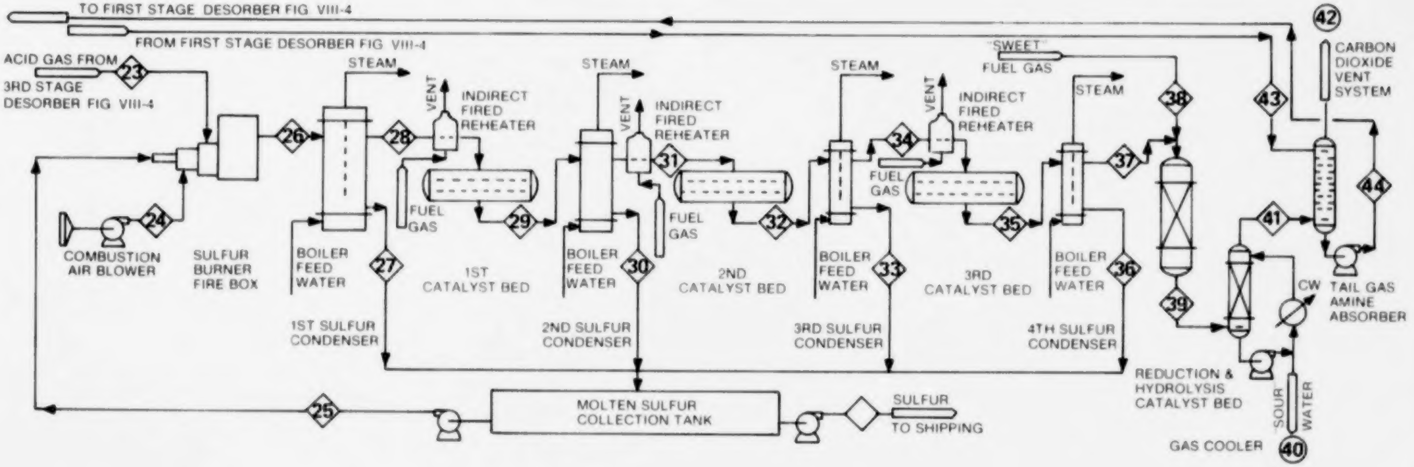
TO FIRST STAGE DESORBER FIG VIII-4
FROM FIRST STAGE DESORBER FIG VIII-4
ACID GAS FROM 3RD STAGE DESORBER FIG VIII-4
23
24
COMBUSTION AIR BLOWER
SULFUR BURNER FIRE BOX
26
STEAM
BOILER FEED WATER
1ST SULFUR CONDENSER
27
28
VENT
INDIRECT FIRED REHEATER
FUEL GAS
1ST CATALYST BED
29
STEAM
BOILER FEED WATER
2ND SULFUR CONDENSER
30
VENT
INDIRECT FIRED REHEATER
31
FUEL GAS
2ND CATALYST BED
32
STEAM
BOILER FEED WATER
3RD SULFUR CONDENSER
33
34
VENT
INDIRECT FIRED REHEATER
FUEL GAS
3RD CATALYST BED
35
"SWEET" FUEL GAS
STEAM
BOILER FEED WATER
4TH SULFUR CONDENSER
36
37
38
39
REDUCTION & HYDROLYSIS CATALYST BED
41
GAS COOLER
CW
"SOUR" WATER
40
43
42
CARBON DIOXIDE VENT SYSTEM
44
TAIL GAS AMINE ABSORBER
25
MOLTEN SULFUR COLLECTION TANK
SULFUR TO SHIPPING

Figure 14. Sulfur-Burning Claus Sulfur Recovery System with SCOT Tail-Gas Treatment Unit

2. One-Stage Selective Absorption Followed by Treatment of Acid Gas by Stretford Process (see Appendix C)

As can be seen in Table 35 one stage of selective absorption using MDEA would produce an acid-gas stream containing approximately 3.2% H_2S. This gas is too lean to be effectively processed with a Claus system. However, sulfur can be recovered from gases containing 3.2% H_2S by the Stretford process. Thus a possible option would be to use one stage of selective absorption to remove the sulfur compounds from the gas followed by a Stretford unit to recover the sulfur from the acid gas.

Such a system (see Fig. 15) would have several advantages. The acid gas (stream 11) produced by the selective absorption step would be relatively clean, that is, free of hydrocarbons. Thus a much higher quality sulfur would be produced since many problems inherent with the Stretford process relative to impurities in the feed gas would be alleviated. The MDEA absorber would remove most of the organic sulfur compounds, COS, CS_2 and mercaptans, but they would pass through the Stretford absorber and end up in the CO_2 stream (16) discharged to the atmosphere.

The volume of acid gas (stream 11) fed to the Stretford unit would be reduced to about 535 sm^3m or about 7.6% of the original volume of the raw gas (stream 3). However, since stream 11 contains essentially the same amount of H_2S as stream 3, the amount of Stretford solution circulated; therefore except for the absorber the size of the Stretford equipment required would be the same as that for the Stretford direct-absorption case. Thus there is no cost advantage in this system over a Stretford direct system.

The estimated overall sulfur reduction calculated for the total desulfurization train is in the range of 98.0 to 99.3%, depending on the quantity of organic sulfur in the gas.

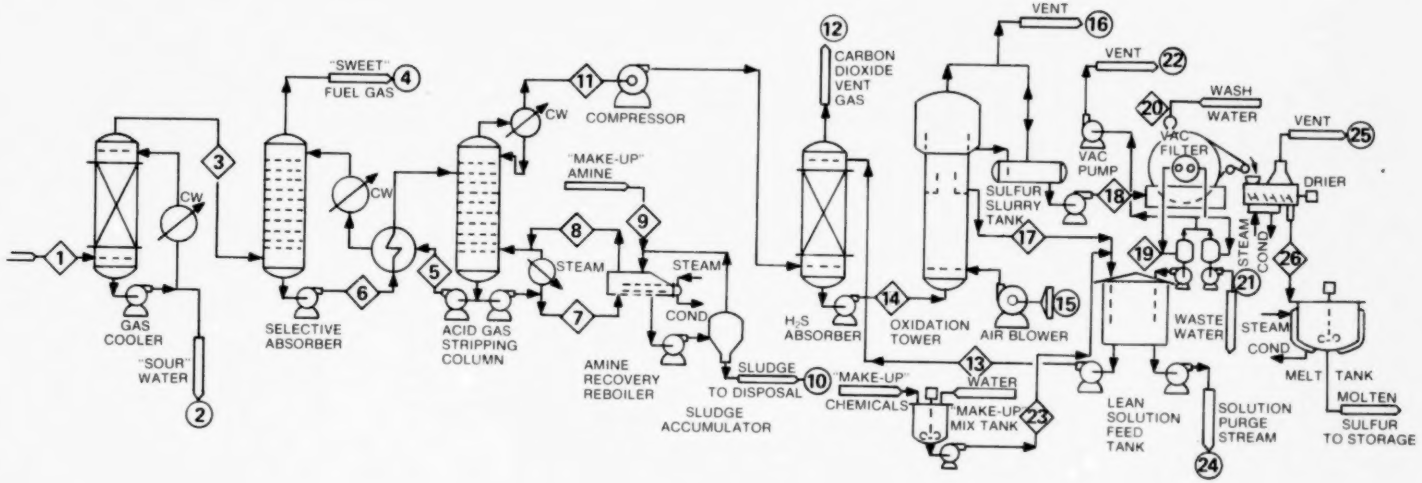
1
GAS COOLER
CW
"SOUR" WATER
2
3
SELECTIVE ABSORBER
"SWEET" FUEL GAS
4
CW
6
5
ACID GAS STRIPPING COLUMN
CW
11
COMPRESSOR
STEAM
8
7
"MAKE-UP" AMINE
9
STEAM
COND
AMINE RECOVERY REBOILER
SLUDGE ACCUMULATOR
SLUDGE TO DISPOSAL
10
12
CARBON DIOXIDE VENT GAS
H_2S ABSORBER
14
OXIDATION TOWER
AIR BLOWER
15
13
"MAKE-UP" CHEMICALS
WATER
"MAKE-UP" MIX TANK
23
VENT
16
SULFUR SLURRY TANK
17
VENT
22
VAC PUMP
18
20
WASH WATER
VAC FILTER
19
21
STEAM
COND
WASTE WATER
LEAN SOLUTION FEED TANK
SOLUTION PURGE STREAM
24
VENT
25
DRIER
26
STEAM
COND
MELT TANK
MOLTEN SULFUR TO STORAGE

Figure 15. One-Stage MDEA Selective Absorption System with Stretford Sulfur Recovery Unit

3. The Diamox Process (See Appendix D)

The Diamox process is a commercially proven process developed jointly by Mitsubishi Chemical Industries (MCI) and Mitsubishi Kakoko Kaisha (MKK), both of Japan, for desulfurizing coke-oven gas. Five facilities employing the process have been built, and their performance has been excellent. MCI reports[20] that the Diamox plants have achieved coke-oven gas desulfurization to levels as low as 13.7 to 18.3 grams of H_2S per 100 sm^3 (about 95 to 126 ppmv). The Ralph M. Parsons Company of Pasadena, California, is the licensee for the process in the United States.

The Diamox process is particularly applicable for removal of H_2S from gases containing ammonia since ammonia is used as the absorbent in the Diamox solution. Ammonia present in the raw gas is absorbed to generate the Diamox solution, and consequently no chemicals are required for the process. Once the Diamox solution is saturated with ammonia, additional ammonia will not be absorbed but instead will pass through with the treated gas. Additional ammonia scrubbers must be added if ammonia has to be removed from the treated gas.

A large part of the proprietary design of the Diamox process is embodied in the design and operation of the absorber and stripping towers and the temperature and solution concentrations maintained throughout the system.[22] The process was developed to selectively absorb H_2S from coke-oven gas with greatly improved removal effectiveness. Up to 98% H_2S removal has been obtained in commercial applications of the process compared to removals of only 90% achieved by conventional processes using ammonical solutions. Selectivity ratios of up to 9.4 have been obtained by the process based on data reported by Hiraoka, Tanaka, and Sudo.[23] Organic sulfur compounds, however, are not appreciably removed.

High-quality, 99.9% pure, bright-yellow sulfur can be recovered from the acid gas produced by the Diamox process since the concentration of ammonia, hydrocarbons, and other contaminants in the acid gas is extremely low.

A simplified flow diagram of the process is shown in Fig. 16. The Diamox process operates as follows. The incoming raw gas (stream 1) is cooled to about 52°C by direct contact with circulating water in a wash tower. Water, with a small amount of absorbed ammonia, and a small quantity of hydrocarbons condensed from the gas are purged from the system (stream 2) and sent to foul-water treatment. Cooling to 52°C permits the bulk of the ammonia to pass through with the cooled gas. The cooled gas (stream 3) then enters the H_2S absorber, where it countercurrently contacts the freshly stripped, lean ammoniacal solution. Nearly all the H_2S and a portion of the CO_2 are absorbed before the treated gas (stream 4) exits from the top of the absorber. The rich solution (stream 5) enters the acid-gas stripper, where the absorbent solution is heated to expel the absorbed acid gases. The stripped or lean absorbent (stream 6) is cooled and then returned to the H_2S absorber; the stripped acid gas (stream 9) is sent to the Claus unit for recovery of sulfur.

A small amount of solution (stream 7) is purged from the recirculating absorbent solution to control buildup of impurities and then is sent to foul-water treatment.

The goal of obtaining a high degree of sulfur removal conflicts with that of simultaneously obtaining high H_2S selectivity; one goal must be compromised to obtain the other. To obtain a high degree of desulfurization the partial pressure of H_2S in the absorbent must be low and the acid-gas concentration in the regenerated lean solution must be at the lowest possible level. Thus large amounts of solution must be circulated through the absorber and greater amounts of utilities consumed in regenerating and recirculating the solution.

The system proposed for the model oil-shale gas disulfurization plant is based on a spray tower absorber with six absorption stages (see

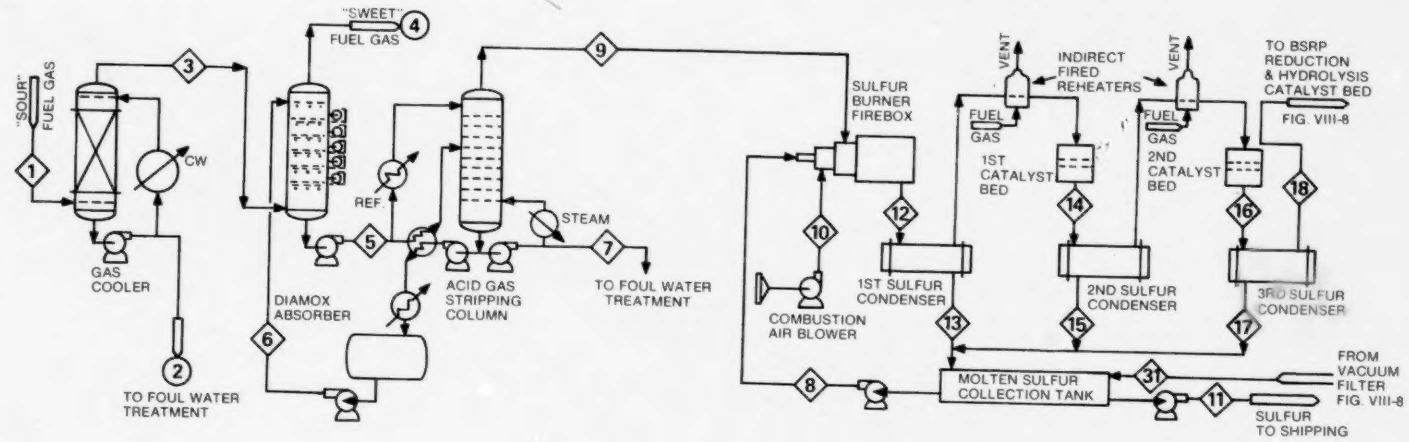
"SOUR" FUEL GAS
1
GAS COOLER
CW
2
TO FOUL WATER TREATMENT
3
"SWEET" FUEL GAS
4
DIAMOX ABSORBER
6
REF.
5
ACID GAS STRIPPING COLUMN
STEAM
7
TO FOUL WATER TREATMENT
9
SULFUR BURNER FIREBOX
10
COMBUSTION AIR BLOWER
8
12
1ST SULFUR CONDENSER
13
FUEL GAS
VENT
INDIRECT FIRED REHEATERS
1ST CATALYST BED
14
2ND SULFUR CONDENSER
15
FUEL GAS
VENT
2ND CATALYST BED
16
3RD SULFUR CONDENSER
17
18
TO BSRP REDUCTION & HYDROLYSIS CATALYST BED
FIG. VIII-8
MOLTEN SULFUR COLLECTION TANK
31
FROM VACUUM FILTER FIG. VIII-8
11
SULFUR TO SHIPPING

Figure 16. Diamox Process with Claus Sulfur Recovery System

Appendix D).[20] The high CO_2 content results in increased CO_2 absorption. Calculations indicate that the H_2S content of the treated gas will be about 63 ppmv and that the acid gas stripped from the rich Diamox solution in the acid-gas stripper contains about 6 mole % H_2S.[20] This equates to an H_2S removal of 97.9% while achieving a selectivity ratio of 4.7. With the gas assumed to contain COS in the range of 10 to 50 ppmv the overall sulfur removal achievable would be 96.3 to 97.6%. The acid gas is fed to a Claus sulfur recovery unit for conversion of the H_2S to elemental sulfur (Fig. 16). The Claus unit tail-gas feeds to a Beavon sulfur removal process (BSPR) for final sulfur recovery (Fig. 17). The BSPR unit was chosen due to the large amount of CO_2 in the acid gas.

The Beavon sulfur removal process for treatment of Claus plant tail gases consists of two main steps: catalytic hydrogenation and hydrolysis of all sulfur species to H_2S and conversion of the H_2S to elemental sulfur by the Stretford process.

The overall sulfur recovery in the Claus and BSRP units is 99.8% percent.[20] The estimated overall sulfur reduction calculated for the total desulfurization train is about 96.1 to 97.4%, depending on the quantity of organic sulfur in the gas.

The Diamox process, while suitable for coke-oven gas containing large amounts of ammonia, carbon dioxide, and hydrogen cynide, is only marginally capable of processing oil-shale gas because the ratio of CO_2 to H_2S in the gas is very high. The process would not be capable of producing an acid gas of sufficient H_2S content for effective operation of the Claus system for most direct-fired oil-shale retort gases without considerable sacrifice of H_2S removal effectiveness.

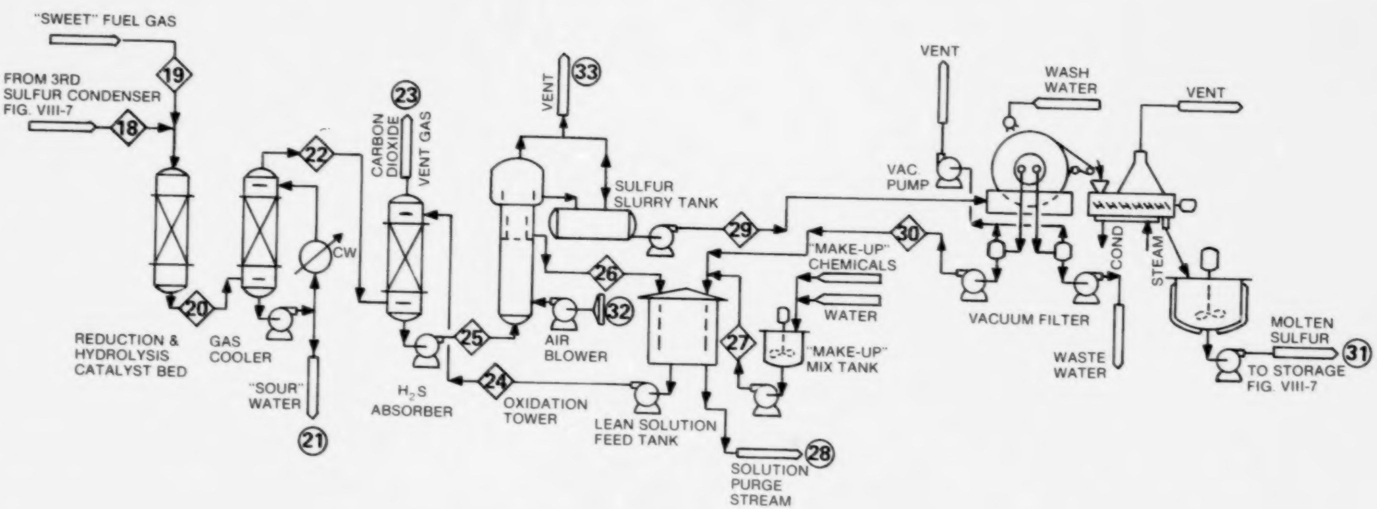
"SWEET" FUEL GAS
FROM 3RD SULFUR CONDENSER FIG. VIII-7
18
19
20
REDUCTION & HYDROLYSIS CATALYST BED
GAS COOLER
CW
22
"SOUR" WATER
21
23
CARBON DIOXIDE
VENT GAS
H_2S ABSORBER
25
24
OXIDATION TOWER
VENT
33
SULFUR SLURRY TANK
26
AIR BLOWER
32
LEAN SOLUTION FEED TANK
29
"MAKE-UP" CHEMICALS
WATER
27
"MAKE-UP" MIX TANK
SOLUTION PURGE STREAM
28
30
VENT
VAC. PUMP
WASH WATER
VACUUM FILTER
WASTE WATER
VENT
COND
STEAM
MOLTEN SULFUR
TO STORAGE FIG. VIII-7
31

Figure 17. BSRP Tail-Gas Treatment Unit

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an *additional* reference is required for only a certain *portion* of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

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IX. COST COMPARISON OF CANDIDATE PROCESSES

Estimated capital and operating costs and cost-effectiveness data for the candidate processes described in Sect. VIII are presented in this section. The estimates were based on a hypothetical direct-fired oil-shale plant processing 45,450 tonnes of shale per day and producing 10.2 million sm^3d of gas having the composition shown in Table 34 Material balance flow sheets were developed for each of the selected candidate processes. The major equipment components were defined and sized and the capital and operating costs estimated.

The estimated capital and operating costs and net annualized cost of the various options evaluated are given in Table 37. The material balance flow sheets and a summary of the equipment requirements and cost estimate details for each process are given in Appendices A, B, C, and D.

The estimated costs are based on a new-plant installation and represent the total investment, including all indirect costs such as engineering and contractors' fees and overheads, required for the purchase and installation of all equipment and material to provide a facility as described. These are battery-limit costs and do not include provisions for bringing utilities, services, or roads to the site; backup facilities; land; required research and development; or process piping interconnections that may be required within the process that generates the gas fed to the desulfurization systems.

Capital cost estimates were developed by summation of installed capital costs for the individual components of each system. These installed capital costs are based on IT Enviroscience experience adjusted to the January 1980 basis. In addition to the sum of the itemized capital costs a contingency allowance of 20% is included in overall capital cost estimates.

Table 37. Estimated Capital and Operating Costs for Fuel-Gas Desulfurization Options[a]

	Costs				
Item	Stretford Direct Process with Purge Stream Disposal[b]	Stretford Direct Process with Purge Stream Recovery[c]	1-Stage MDEA Selective Absorption with Stretford Sulfur Recovery[d]	3-Stage MDEA Selective Absorption with Claus Sulfur Recovery[e]	Diamox Process with Claus Sulfur Recovery[f]
Capital cost[g]	$13,322,000	$14,840,000	$17,200,00	$15,551,000	$32,741,000
Operating cost (per year)					
Chemical makeup	$1,088,000	$ 911,000	$ 1,190,000	$ 24,000	$ 84,000
Steam	70,000	107,000	3,812,000	7,183,000	11,530,000
Power	303,000	345,000	234,000	158,000	1,618,000
Fuel gas		328,000			
Cooling water	526,000	578,000	1,261,000	1,545,000	1,950,000
Waste treatment	No cost	Neg.	No cost	Neg.	No cost
Operating labor	600,000	720,000	630,000	480,000	480,000
Maintenance, capital recovery and misc.	3,864,000	4,304,000	4,988,000	4,510,000	9,495,000
Total operating cost	$6,451,000	$7,293,000	$12,115,000	$13,900,000	$25,157,000
Sulfur recovery credit (per year)	$1,083,000	$1,116,000	$1,130,000	$1,171,000	$1,150,000
Net annualized cost					
Per year	$5,368,000	$6,177,000	$10,985,000	$12,729,000	$24,007,000
Per ton of shale	0.29	0.34	0.60	0.70	1.32
Per barrel of oil	0.50	0.57	1.01	1.17	2.21

[a] For 360-million-scfd plant based on Paraho gas (see Table VIII-1). [b] Stretford purge stream disposal at no cost. [c] Stretford purge stream incinerated and gases, water, and decomposed sodium salts recycled. [d] Sulfur recovered with Stretford system. [e] Sulfur recovered with Claus system with SCOT tail-gas treatment. [f] Sulfur recovered with Claus system with BSRP tail-gas treatment. [g] Includes process royalty fee.

The actual cost of applying any of these options at any specific location could vary considerably from that given here. The purpose of these estimates was to determine the relative cost differences between the various options. Since the estimates for each of the options evaluated were calculated on the same bases, the relative costs of applying the systems should be in the order shown.

Special cautions must be used if an attempt is made to extrapolate from the cost-effectiveness data given since these costs will be largely dependent on the composition and volume of gases to be treated, on the oil yields, and on the cost factors that are pertinent to installation site.

For desulfurization of gases from direct-fired oil-shale retorts the Stretford process is the most cost-effective system. For the model case shown the cost of sulfur removal would be about $0.50 per barrel of oil produced, which is less than half that projected for the better of the indirect sulfur-removal processes. The model case is based on Paraho gas, which has the lowest CO_2/H_2S ratio (76:1) of any gas considered for the direct-fired retorts. For direct-fired gases having higher CO_2/H_2S ratios the gap between the cost of applying the Stretford process and the indirect desulfurization processes would be expected to increase, making the other options even less competitive. For gases with lower CO_2/H_2S ratios the indirect sulfur-removal processes would become more competitive. For gases from indirect-heated retorts, such as Tosco with a CO_2/H_2S ratio of 4.1:1, the indirect processes could very well become more cost effective than the Stretford process.

The operating costs given are based on the assumption that there is no cost for wastewater treatment. The sour water stream in each case would be stripped of H_2S and processed for recovery of hydrocarbon and ammonia by-products. The cost of this treatment, which is partly offset by the valve of the by-products recovered, was assumed to be equal in each case and therefore is not included. The Stretford purge streams, containing essentially dissolved salts, were assumed to be acceptable for disposal through moisturizing of the spent shale at no cost. The cost of evaporating the purge streams to recover dissolved salts would be about $557,000/yr ($0.05/bbl) for the Stretford direct systems and about $37,000/yr ($0.003/bbl) for the BSRP system used for treatment of the tail gases from the Diamox process Claus unit.

The cost of a Stretford system incorporating a purge-stream reductive-incineration system for recovery and recycle of salts is also given in Table IX-1. This option would result in a sulfur removal cost of about $0.57 per barrel of oil produced, which is about $0.07 more per barrel than the case based on disposal of the purge stream at no cost.

X. RECOMMENDED AVAILABLE H_2S CONTROL TECHNOLOGY

The Stretford direct fuel-gas desulfurization process was recommended as the most applicable technology for removal of sulfur from direct-fired oil-shale retort gases. The basis for this selection is as follows.

A. ADAPTABILITY

Gases from direct-fired retorts have a low heating value (1.52 to 4.13×10^6 joules/sm^3) because of the large amount of nitrogen, carbon dioxide and other inert gases in the gas. It is not economically feasible to upgrade the quality of the gas so that it will meet pipe-line quality standards and can therefore be sold as a substitute for natural gas. Practical uses of the gas are limited to combustion for generating process heat or electrical power, for which purpose only the ammonia and sulfur need to be removed.

The large volumes of gas that must be processed in a typical oil-shale plant will limit the application of desulfurization technology to high-capacity, continuous-liquid-phase processes. Since CO_2 is absorbed to some extent by all liquid-phase processes, the high CO_2/H_2S ratio of the gas limits the selection to those processes that can selectively absorb sulfur compounds in the presence of large amounts of CO_2. Of those direct processes that selectively remove H_2S by direct conversion of the H_2S to elemental sulfur, the Stretford process is the most effective. Of those indirect processes that selectively remove H_2S by separating the H_2S as a concentrated acid-gas stream, the Selectamine or the Adip processes using MDEA as the absorbent, the Benfield, the Selexol, and the Diamox processes were selected as the most effective in their separate process classifications. These processes were than considered as candidates for further study.

B. OPERATIONAL REQUIREMENTS

Oil-shale retort gases are produced at near-atmospheric pressures; thus those processes requiring the gas to be at a high pressure (Benfield and Selexol) were eliminated since compression of the gas for the purpose of desulfurization could not be economically justified.

The Claus process is used to recover sulfur from the acid gas produced by the indirect sulfur-removal processes. The large amount of CO_2 in the gas makes the best of the indirect process only marginally capable of producing an acid gas rich enough in H_2S for processing by the Claus process. Thus to apply these processes, multiple stages of selective absorption would be required to handle the gas produced by many of the direct-fired retorts.

The Stretford direct process, on the other hand, is only minimally affected by the quantity of CO_2 in the gas and therefore is adaptable to the full range of gases produced by direct-fired retorts.

A Stretford plant incorporating a venturi absorber can operate with a wide-volume turndown range. The system capacity is limited by the maximum design-basis throughput capacity of the sulfur. The quantity of sulfur in the gas can drop to nearly zero without affecting the sulfur removal efficiency.

The indirect selective sulfur-removal processes have only limited turndown capability. The selectivity of the process (preferencial absorption of H_2S over CO_2) is largely achieved through control of the absorption kinetics. Therefore large changes in absorber gas or liquid throughput can adversely affect the selectivity achieved and consequently the composition of the acid gas produced. The Claus process has a limited range of operation and can be upset by large variations in the composition of the acid-gas feed. The wide range and constant variation of the CO_2/H_2O ratio of gases from in-situ retorts would be very difficult to handle with an indirect selective absorption system.

C. SULFUR-REMOVAL EFFECTIVENESS

A very high degree of H_2S removal can be achieved by all the candidate processes discussed. Generally the higher the amount of sulfur that must be removed the more it will cost to install and operate the desulfurization train. The cost of applying these systems then becomes the overriding factor rather than the ultimate sulfur-removal effectiveness.

Except for the Diamox process all the candidate processes are capable of removing H_2S down to about 10 ppmv. However, organic sulfur compounds, principally COS, which exists in only trace amounts in the gas, are not significantly removed or are only partly removed by the various process. Table 38 gives the variation in process effectiveness with the amount of COS in the raw gas. Current Colorado emission standards limit sulfur emissions to an equivalent of 0.3 lb of SO_2/bbl of crude oil produced. The estimated SO_2 equivalent emissions for each of the candidate process are shown in Table 38.

D. RELATIVE COSTS

The relative costs of the candidate processes studied are given in Table 39.

For desulfurization of gases from direct-fired oil-shale retorts the Stretford process is the most cost-effective system. The cost ratios shown, based on Paraho gas, would be expected to increase for other direct-fired-retort gases having higher CO_2/H_2S ratios.

The three-stage MDEA process produces the highest degree of sulfur recovery, whereas the Stretford process produces the lowest. In the latter process sulfur recovery losses result from formation of sodium thiosulfate in the Stretford solution.

E. WASTES GENERATED

The Stretford process produces a concentrated waste stream containing about 22% dissolved solids. The MDEA selective absorption systems produce a small quantity of concentrated sludge from the solution reclaimer. The quantities of these wastes are as follows:

Table 38. Variation of Process Effectiveness with Amount of COS in Raw Gas[a]

			Total Sulfur		Estimated Overall Emissions				
					Total Sulfur		SO_2 Equivalent		
	H_2S Remaining (ppmv)	COS Reduction (wt %)	Reduction (wt %)	Remaining (kg/hr)	(kg/hr)	(tonnes/day)	(kg/hr)	(kg/bbl of oil)	Overall Sulfur Reduction (wt %)
Stretford	10	Nil	98.0 - 99.3	19 - 58	19 - 58	0.45 - 1.35	38 - 115	0.02 - 0.05	98.0 - 99.3
MDEA - 1 stage with Stretford	10	60	99.2 - 99.5	13 - 29	20 - 59	0.45 - 0.90	40 - 117	0.02 - 0.05	98.0 - 99.3
MDEA - 3 stages with Claus/SCOT	10	60	99.2 - 99.5	13 - 29	20.4 - 36	0.45 - 0.90	41 - 72	0.02 - 0.04	98.0 - 99.3
Diamox with Claus/BSPR	63	Nil	96.3 - 97.6	70 - 109	75 - 114	1.81 - 2.70	151 - 228	0.07 - 0.11	96.1 - 97.4

[a] Based on a Paraho plant producing 8,000 m^3 of oil per day with COS ranging from 10 to 50 ppmv in the raw gas.

Table 39. Relative Costs of Various Gas Desulfurization Options[a]

Category	Stretford Direct Process with Purge Stream Disposal	Stretford Direct Process with Purge Stream Recycle	1-Stage MDEA Selective Adsorption with Stretford Sulfur Recovery	3-Stage MDEA Selective Absorption with Claus Sulfur Recovery	Diamox Process with Claus Sulfur Recovery
Installed capital cost	1.00	1.11	1.29	1.17	2.46
Utility costs	1.00	1.51	5.90	9.88	16.79
Total operating costs	1.00	1.13	1.88	2.15	3.90
Value of sulfur recovered	0.92	0.95	0.96	1.00	0.98
Net annual cost	1.00	1.15	2.05	2.37	4.47
Cost effectiveness	1.00	1.15	2.04	2.34	4.54

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[a] Based on a plant processing 10.2 million sm^3 of Paraho gas per day. The most effective or least costly option in each category is shown as unity (1.00). The relative costs of the other options are shown as a ratio to the most effective or least costly system.

Stretford direct	7570 ℓ/day
3-stage MDEA with Claus/SCOT	37.85 ℓ/day
1-stage MDEA with Stretford	7570 ℓ/day
Diamox with Claus/BSRP	246 ℓ/day

These estimates do not include sour water, which would be processed for hydrocarbon and ammonia recovery prior to disposal. The quantity of sour water in each case would be about the same (1.13×10^6 to 1.51×10^6 ℓ/day).

F. RELIABILITY

All the candidate processes were commercially developed and are used in various applications around the world. The stretford process has been widely applied, with more than 80 commercial plants currently in operation.

As with any process application operating problems can develop, and if the system is misapplied or poorly designed, the problems can be insurmountable. The principal problems reported by Stretford users are plugging of packed absorbers by precipitated sulfur; loss of scrubbing performance, when processing gases with large percentages of CO_2, because CO_2 is absorbed and the solution pH is consequently lowered; and poor-quality sulfur as the result of hydrocarbon and other contaminants in the sulfur.

The process licensors feel confident that with proper design and through use of proprietary Stretford chemicals these problems can be managed.

XI. PILOT-PLANT DESIGN

A. INTRODUCTION

Gases produced from direct-fired oil-shale retorting processes are sufficiently different from gases previously encountered in commercial application of gas-desulfurization systems that the technology cannot be simply transferred. Application of the Stretford process or any other process to the treatment of these gases would extend the technology of the process into areas in which no analogous experience is available. Many questions need to be answered before the process can be applied with confidence to a full-scale commercial shale-oil production facility.

The primary function of the pilot plant would be to test the technical feasibility of the Stretford process for treatment of gases from oil-shale retorting processes, to prove the engineering assumptions and calculated forecasts made for the process, and to generate scaleup design data for commercial applications of the process.

The pilot plant should be portable and capable of operating on a slip stream from any of the currently operating or proposed direct-fired oil-shale retorting facilities in the United States. The unit should be flexible enough to accommodate inputs from surface and in-situ retorts with flow rates ranging from 2.83 to 28.3 sm^{3}m while retaining adequate design efficiencies; if possible it should have sufficient turndown capability to also operate on gases from indirect-heated retorts.

The pilot plant would be a Stretford system based on the current state-of the-art technology for commercial applications of the process. The unit should be the smallest size that will operate on actual shale-oil retort-gas feeds under typical plant constraints and still permit study of the process dynamics.

B. SIZING OF PILOT PLANT

Based on the gas characterization data compiled the CO_2/H_2S mole ratios are widely separated in the gases from indirect- and direct-fired retorting processes, and it is unlikely that a fixed-size pilot plant could handle the full range of gases from both types of retorts. With direct-fired retorts, either above or below ground where combustion occurs within the retort, gas rates vary from 68.5 to 405 sm^3/tonne of shale processed and the H_2S content varies from 0.07 to 0.30 vol % (DG). The CO_2/H_2S molar ratio varies from 76 to 165 or more.

For indirect-heated retorts, where heat to the retort is generated externally, the gas rates vary from 27.2to 35.0 sm^3/tonne of shale processed and the H_2S content varies from 3.8 to 4.1 vol % (DG). The CO_2/H_2S molar ratio varies from 4.3 to 5.0.

Thus for a volume turndown ratio of 10 (28.3 to 2.83 sm^{3}m) the pilot plant would have to have a sulfur turndown capability of 586 to 1 if the H_2S content of the gas ranged from 0.07 to 4.1 vol %. If the plant were designed for only gases from direct-fired retorts, a sulfur turndown capability of 34 to 1 would be required. Similarly if the plant were designed for only gases from indirect-heated retorts, a sulfur turndown capability of 11 to 1 would be required. However, if the gas volume were decreased as the sulfur content was increased, then a sulfur turndown capability of only 6 would be required to handle the full range of gases from both direct and indirect oil-shale retorts (i.e., 2.83 sm^{3}mof gas from an indirect-heated retort containing 4.1% H_2S to 28.3 sm^{3}m of gas from a direct-fired retort containing 0.07% H_2S).

In reality the Stretford system is limited in both gas throughput capacity and sulfur loading capacity. Therefore to provide maximum turndown capability, the pilot plant should be sized to handle the maximum case for direct-fired retorts (28.3 sm^{3}m of Paraho gas containing 0.30 vol % H_2S). Gases containing less sulfur can be handled up to 28.3 sm^{3}m since the system is capable of operating with reduced sulfur loadings. For gases containing more sulfur, the gas volume can be turned down to within the limits of the absorber operation while maintaining maximum sulfur loading.

C. DUTY SPECIFICATIONS

The pilot plant should be designed primarily to remove H_2S from oil-shale gas produced by direct-fired retorts. The maximum capacity of the pilot plant should be 28.3 sm^3m of feed gas. The maximum sulfur capacity should be 6.6 Kg of sulfur per hour based on a loading of 800 ppmw of hydrosulfide ion (HS^-) in the solution. The plant should be capable of reducing the H_2S content of the gas to 10 ppmv or less, and CO_2/H_2S ratios as high as 200 to 1.

The pilot plant should include equipment for cooling the feed gas from 60° to 32°C and for removing the ammonia before the feed gas enters the Stretford absorber. The pilot-plant design should include only those equipment components, instruments, and controls necessary for safe operation of the equipment and as required to adequately test and demonstrate the Stretford process and to carry out the intended research program. Most of the data required for determining the performance and operation of the system would be obtained by manual sampling and laboratory analysis of the process streams.

D. RECOMMENDED SYSTEM

1. Basis of Design

The bases for designing and sizing the pilot-plant components are as follows:

Gas characteristics	
Maximum volume (dry gas)	28.3 sm^3m
Pressure	Atm
Temperature	60°C

Critical components	
H_2S	0.3 vol %
CO_2	22.8 vol %
NH_3	0.7 vol %
H_2O	Saturated
Cooling water temperature	21°C
Sour-water treatment	Not included
Sulfur recovery	Disposal as wet cake
Stretford solution sulfide loading	800 ppmw

2. Description of Process

A material balance flow sheet for the Stretford pilot plant is shown on Fig. XI-1. The idealized process reactions are as follows:

Reaction 1

$$Na_2CO_3 + H_2S \longrightarrow NaHS + NaHCO_3$$

Reaction 2

$$4NaVO_3 + 2HaHS + H_2O \longrightarrow Na_2V_4O_9 + 4NaOH + 2S$$

Reaction 3

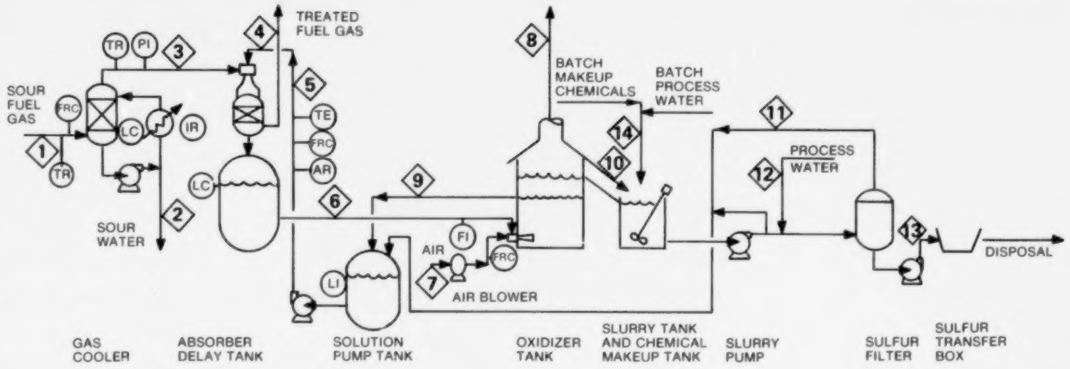
$$Na_2V_4O_9 + 2NaOH + 2ADA^* \longrightarrow 4NaVO_3 + 2ADA\ (reduced)$$

Reaction 4

$$2ADA\ (reduced) + O_2 \longrightarrow 2ADA^* + H_2O$$

*Anthraquinone disulfonic acid.

The sour fuel-gas feed (stream 1) enters the gas cooler, where it is cooled by direct contact with circulating water solution. The flow rate of feed gas is controlled to the rate set for the test and is continually recorded. As the gas is cooled, a large portion of the water and most of the ammonia are removed (stream 2). Heat is ex-


TREATED FUEL GAS
SOUR FUEL GAS
SOUR WATER
BATCH MAKEUP CHEMICALS
BATCH PROCESS WATER
PROCESS WATER
AIR
AIR BLOWER
DISPOSAL
TR
PI
FRC
LC
IR
TE
AR
LI
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1
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5
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7
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9
10
11
12
13
14
GAS COOLER
ABSORBER DELAY TANK
SOLUTION PUMP TANK
OXIDIZER TANK
SLURRY TANK AND CHEMICAL MAKEUP TANK
SLURRY PUMP
SULFUR FILTER
SULFUR TRANSFER BOX

lb/hr \ Stream No.	1	2	3	4		5	6	7	8	9	10	11	12	13	14
H_2	15.10		15.10	15.10	Oxygen			36.70	29.40						
O_2	2.29		2.29	2.29	Nitrogen			120.90	120.90						
N_2	2825.53		2825.53	2825.53	NaHS		25.57*								
CO	110.68		11068	110.68	Water	20000.00	20006.00	2.80	4.80	19832.00	168.00	92.13	8.79	14.60	5.81
CO_2	1586.67	48.67	1538.00	1538.00	Sulfur		a			—	14.60	—		24.60	
CH_4	54.72		54.72	54.72	Vanadate	114.90	114.90			113.90	0.96	0.65		0.03	0.03
C_2H_4	29.28		29.28	29.28	ADA	214.90	214.90			213.10	1.80	1.02		0.06	0.06
C_2H_6	26.61		26.61	26.61	EDTA	54.00	54.00			53.50	0.45	0.26		0.02	0.02
C_3H_8 }	48.38		48.38	48.38	Iron (Soluble)	2.00	2.00			1.98	0.02	0.01		Trace	Trace
C_3H_6 }					$NaHCO_3$	1016.00	1055.60			1046.70	8.86	5.53		0.31	
C_2S	50.55		50.55	50.55	Na_2CO_3	59.90	10.00			9.92	0.08	0.23		Trace	0.29
C_3S }	68.54	Trace	68.54	68.54	$Na_2S_2O_3$	3822.90	3824.00			3791.90	32.10	18.42		1.11	
C_4S + }	–	of H-C's													
H_2S	16.17	0.12	16.05	00.54	Hydrocarbons		Trace		Trace						
NH_3	18.83	18.83	Trace	–											
H_2O	712.03	581.87	130.16	130.16											
COS															
CS_2															
RSH															
Total, lb/hr	5565.38	649.49	4915.89	4899.89	Total, lb/hr	25285.00	25301.00	160.40	155.10	25063.00	226.87	118.25	8.79	40.73	6.21
Total, SCFM, DG	1000.00		986.00		Total, SCFM			34.50							
Temp	140°F	90°F	90°F		Total, gpm	42.20									
pH															

*H_2S is in transition between [HS] and Sulfur

Figure 18. Material Balance Flowsheet for Pilot Plant

tracted by circulating the water solution through a water-cooled heat exchanger.

The temperatures of the incoming sour gas, the cooled gas, and the cooling water discharge streams are continually monitored. The sour water (stream 2) is discharged. Treatment of the sour water is outside the scope of the pilot plant.

The cooled gas (stream 3) then enters the ejector-venturi gas absorber at about 90°F. The ejector-venturi absorber (see Appendix E) operates on the jet principle, in which the Stretford solution is under pressure to create a draft and simultaneously provide intimate contact between the liquid and gas as it passes through the venturi. On contact with the alkaline Stretford solution, which is an aqueous solution containing sodium carbonate, sodium metavanadate, and anthraquinone difulfonic acid (ADA), the H_2S dissolves rapidly and forms a small concentration of hydrosulfide ion (reaction 1). Sodium carbonate in the solution enters into the reaction and provides a buffer to prevent rapid pH changes as the acid gases are absorbed.

The solution will absorb some CO_2, resulting in formation of sodium bicarbonate and consequent lowering of the pH until equilibrium is reached with respect to the level of CO_2 in the gas. The pH of the Stretford solution will therefore be a function of the level of CO_2 in the gas. At the point when equilibrium is reached, there must be sufficient Na_2CO_3 remaining to convert all the H_2S in the solution to hydrosulfide ions.

For gases with large CO_2/H_2S ratios the pH of the solution may be sufficiently lowered to affect the absorption rate of H_2S. In that case addition of proprietary additives to the solution may be required for the hydrosulfide loadings to be as high as 800 ppm.

The venturi discharges into a mist eliminator, where gases are separated from the liquids. The treated gas (stream 4), in which essentially all the H_2S has been removed, will be returned to the oil-shale process. The separated liquid will flow into the delay tank.

The sodium metavanadate in the solution readily reacts with the hydrosulfide to produce elemental sulfur (reaction 2) and a reduced form of vanadium. Sufficient residence time is provided by the delay tank to assure that any remaining hydrosulfide in the solution is reacted so as to prevent hydrosulfide ions from entering the oxidizer and becoming oxidized to sodium thiosulfate, an undersirable, stable, by-product.

Flow (stream 6) from the delay tank is by gravity to minimize sticking of the sulfur when the solution is in a transitory Redox stage. A liquid-level controller is provided to control the flow of solution from the delay tank to the oxidizer. The reacted solution containing reduced vanadium and reduced ADA is regenerated in the oxidizer tower according to reactions 3 and 4 by being sparged with an excess of air (stream 7) supplied by a blower. The flow of air can be adjusted so that sulfur particles will properly rise, forming a froth at the surface but allowing the Stretford solution to settle clear of sulfur. The accumulated sulfur froth overflows (stream 10) to a slurry tank. Trace amounts of volatile hydrocarbons that may be absorbed in the Stretford solution will be stripped by the air rising in the oxidizer. A hood provided over the oxidizer tank will lift and direct the discharge gases (stream 8) away from the operators.

The regenerated Stretford solution (stream 9) is essentially free of sulfur and is returned to the solution pump tank. The solution pump tank is sized to hold all the required solution when the pilot plant is shut down.

The regenerated solution (stream 4) is then pumped back to the venturi absorber at a preset and controlled rate. The flow rate, pH, and temperature of the solution are continually monitored and recorded.

Equipment for handling the sulfur slurry has been reduced to the minimum in an attempt to keep the cost of the pilot plant to a minimum and yet provide sufficient capability to test and demonstrate the Stretford process.

The sulfur produced will be disposed of as a wet cake. A sulfur filter (see Appendix E) operated on a batch basis will filter the sulfur from the slurry. The filtrate solution (stream 11) is returned to the solution pump tank. The wet sulfur cake accumulated in the filter will be discharged to a transfer box, which is sized for 4 days of operation at maximum utilization. The amount of Stretford solution lost with discharge of the wet sulfur cake (stream 13) should be sufficient to keep the buildup of sodium thiosulfate in balance. The cost of Stretford chemicals lost in the sulfur cake at the pilot level of operation is not a significant economic factor. The filter system is arranged so that the filter cake can be rinsed (stream 12) before is is discharged.

3. Turndown Capability

The described capacity of the pilot plant (6.6 Kg of sulfur/hr) is based on an average solution loading of 800 ppm. Sulfur loadings of 500 to 1000 ppm are commonly achieved. The maximum solution loading obtained will depend on many factors but will largely be a function of the solution pH, which is influenced by the amount of CO_2 in the gas. Solution loadings can be anywhere from zero up to the maximum capacity of the solution, which therefore allows infinite turndown in the quantity of sulfur contained in the feed gas. However, the cost of a Stretford plant is largely a function of the amount of solution that must be circulated, and therefore a goal in piloting the process is to determine the maximum solution loading possible that will result in adequate operation of the system while obtaining a satisfactory level of H_2S removal effectiveness.

The use of the ejector-venturi gas scrubbing system (see Appendix E) affords wide gas turndown capability for the system. Since the flow of gas is motivated by the liquid spray, the scrubbing system functions largely independently of the gas flow rate. The scrubber, which has a maximum gas capacity of 28.3 sm^{3}m, can be turned down to nearly zero. For gases containing larger amounts of sulfur the solution loading can be adjusted by reducing the gas throughput.

By changing the ejector liquid-spray nozzle the rate of liquid circulation can be reduced. Therefore gases with less sulfur can be accommodated while maintaining high solution loadings.

The operation of the pilot plant would approximate that described in Table 40 for various gas feeds.

4. Equipment Description

The pilot plant would be a portable skid-mounted unit, completely assembled with all equipment, controls, and instrumentation required for a complete and operable unit. Utilities and services needed to operate the pilot plant must be supplied at the test site and be field connected.

The maximum demand for services is as follows:

Raw retort gas feed	28.3 sm^{3}m (30.5cm-diam duct)
Treated gas return	28.3 sm^{3}m (30.5cm-diam duct)
Electrical power	30 hp (460 V, 3-phase, H_2)
Process water	0.11 ℓpm
Cooling water	1100 ℓpm
Sour-water disposal	4.9 ℓpm

A list of the major equipment required for construction of the pilot plant is given in Table 41.

E. PRELIMINARY COST ESTIMATE

The total estimated cost of the pilot plant with all equipment, instruments, and controls as described, assembled on skid mountings as a complete and operable unit, is as follows:

Table 40. Approximate Pilot-Plant Operation for Various Gases

Gas	Type of Retort	H_2S (vol %)	Gas Flow (sm^3m)	Sulfur (Kg)	Liquid Flow (ℓpm)	Solution Loading (ppm wt)
Tosco	Indirect	4.12	2.37	6.6	159	800
Union	Indirect	3.82	2.55	6.6	159	800
Paraho	Direct	0.30	32.4	6.6	159	800
Geokinetics	Direct	0.13	31.1	4.3	102	518
Oxy	Direct	0.119	31.1	4.0	102	476

Table 41. . Pilot-Plant Components

Component (1 Each)	Construction Material	Description
	Item No. 100: Gas-Cooler Module (1)	
Gas cooler	Type 304 SS	Complete skid-mounted assembly as follows: packaged column, 76.2cm-diam X 304.8cm straight side, with 122cm of 5.1cm Intalox saddles; vertically mounted; atm pressure, 60°C
Heat exchanger	Type 304 SS shell and tubes	$35.52 m^2$; horizontally mounted; atm pressure, 60° to 32°C.
Circulation pump	Type 316 SS	1136 ℓpm, 30 psig, 10 hp.
Flow control		Gas flow control value with flow sensor transmitter, controller, and recorder
Level control		Liquid-level control valve with sensor, controller, and high- and low-level alarms
Temperature		Multiple-point temperature recorder with temperature sensors
Pressure indicator		Direct-reading pressure gage (in inches of water)
Gas analyzer		Gas/liquid chromatograph for measuring H_2S in gas stream with manual samples
Skid mounting	Steel	As required

Table 41. (Cont'd)

Component (1 Each)	Construction Material	Description
	Item No. 200: Absorber Module (1)	
Venturi scrubber	FRP with type 304 SS nozzle	Complete skid-mounted assembly as follows: 5.1 cm, suction and discharge; 31.1 am^3m at 32°C; 1.27 to 2.54cm water gage draft; .59 ℓpm water solution at 1.2 sp. gr.; 60 psig
Mist eliminator	Steel	681.3ℓ vertical tank with 66 cm--diam X 15.2cm-deep type 304 SS demister pad
Delay tank	Steel	2460 ℓ, 91.4cm diam X 545 cm straight side; vertical tank
Solution pump	Malleable iron	189 ℓ, 60 psig, 3 hp
Flow control		Liquid-flow control valve with flow sensor, transmitter, controller, and recorder
pH monitor		pH sensor, transmitter, and recorder
Level control		Liquid-level control valve with sensor and high-level alarm
Temperature sensor		Temperature sensor, connected to temperature recorder for Item No. 100
Skid mounting	Steel	As required

Table 41. (Cont'd)

Component (1 Each)	Construction Material	Description
	Item No. 300: Oxidizer Module (1)	
Oxidizer tank	Steel	Complete skid-mounted assembly as follows: 45.7 cm-diam X 30.5 cm straight side; vertically mounted, with sludge ring and spout for sulfur slurry; cone hood type of vent top with 366 cm stack
Air blower	Standard	1.42 sm^{3}m, 15 psig, with inlet air filter
Injector	Type 304 SS	Air, 1.05 sm^{3}m at 8 psig; liquid, 159 ℓpm; sp. gr. 1.2
Solution pump tank	Steel	4542 ℓ; 122 cm diam X 366-cm straight side; vertically mounted
Flow control		Air flow control valve with flow transmitter controller and recorder
Sight glass		Liquid-flow sight glass
Level indicator		Liquid-level indicator with low-level alarm
Skid mounting	Steel	As required

Table 41. (Cont'd)

Component (1 Each)	Construction Material	Description
	Item No. 400: Sulfur Module (1)	
Slurry tank	Steel	Complete skid-mounted assembly as follows: 681-ℓ, 76.2cm-diam X 137-cm straight side; open top
Agitator	Steel	Clamp type; mild agitation; 0.25 hp
Slurry pump	Duriron	5.7 ℓ, 45 psig, 0.25 hp
Sulfur filter	Type 304 SS	45.7cm-diam X122cm st. side; vertically mounted plate type; 50 psig
Sulfur sluice pump	Duriron	37.8 ℓpm low head, 0.5 hp
Sulfur transfer box	Steel	2.3m^3 (2271 ℓ); closed dumpster
Skid mounting	Steel	As required

Item-100 gas cooler module	$200,000
Item-200 absorber module	74,000
Item 300 oxidizer module	68,000
Item 400 sulfur handling module	58,000
Total cost (December 1980 capital)	$400,000

If the gas were provided at $22^{\circ}C$, the gas cooler module could be eliminated, in which case the total cost of the system would be about $260,000. The cost of the gas cooler module (Item 100) includes the instrumentation and controls required for proper functioning of the pilot unit. These instruments ($60,000) would be required even if the cooler module were eliminated.

The probable cost range is estimated as follows:

Range	With Cooler	Without Cooler
High	$520,000	$338,000
Probable	400,000	260,000
Low	308,000	200,000

F. ADVANTAGES AND USE OF PILOT PLANT

The primary purposes of a pilot plant are to prove the technical feasibility of the process application and to obtain data needed for scaleup of the process to production-size equipment. If the performance of the pilot plant both at optimum and extreme conditions matched the predicted results and if there were no unreconcilable problems, then commerical application of the process could be carried out with confidence. The advantages to the EPA of piloting the process would be to

1. determine the characteristics of the raw retort gas,
2. determine the characteristics of the treated gas,
3. determine the characteristics of the waste streams,
4. predict the characteristics of controlled emissions,
5. determine the process efficiency and reliability,

6. evaluate transient conditions of startup, normal and emergency shutdown, process upsets, etc.,
7. evaluate the economics of the Stretford process.

Piloting of the process can aid in commercial application of the process by providing demonstration of continuous operation of the system, as well as the following data:

1. Level of H_2S and other sulfur compounds in the treated gas and percentage of overall removal of sulfur compounds by the Stretford process
2. Disposition of COS and other organic sulfur compounds in the feed gas
3. Effects of unsaturated hydrocarbons in the feed gas on process operation and life of the Stretford chemicals
4. Amount of hydrocarbons or other contaminants in the oxidizer vent
5. Quality of sulfur produced
6. Solution sulfur loading versus gas characteristics
7. Rate of thiosulfate formation versus gas characteristics
8. Absorption of CO_2 versus gas characteristics
9. Design parameters for the absorber
    a. HS^- loading in the solution
    b. Thiosulfate concentration
    c. Na_2CO_3 concentration
10. Design parameters for the oxidizer
    a. Ratio of air to sulfur loading
    b. Ratio of air to tank diameter
    c. Height of oxidizer
    d. Characteristics of sulfur froth
11. Design parameters for filter
    a. Filter selection
    b. Pumping rates and pump type
    c. Filtration rates and wash cycles required

    d. Sulfur quality
    e. Washwater evaporation rate required

12. Design parameters for gas cooler
    a. NH_3 and H_2S absorption versus gas characteristics
    b. Characteristics of sour water

13. Evaluation of corrosion problems and materials of construction

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APPENDIX A

STRETFORD DIRECT PROCESS

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PAGE NUMBER
EPA-287 (Cin)
(4-76)

PRELIMINARY CAPITAL - DETAIL SHEET

SHEET 1 OF 6

PROJECT: STRETFORD DIRECT PROCESS
JOB NUMBER: 9212
PHASE: PRE-1
CASE: Case A
BY:
DATE: 1-31-80
EF NUMBER:
SECTION NUMBER & NAME:
SECTOR NUMBER & NAME:

FACTORS → BASE X ESC. X CAPACITY XQUANT. X [MATERIAL + CONDITION + COMPLEXITY] = M$(19)

ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION	
101	Gas Coolers	6	304 St.Stl	12'Φx42' Bl to Bl., 10 PSI 18' Packed section 2000 ft^3 - 3 1/2"Φ Pall Rings	
102	Cooler Cir. Pumps	6	304 St.Stl	1000 GPM, 100' HD, 40 HP	
103	Exchangers	6	304 St.Stl	5000 ft^2, U Tube, 14' LG Tube	
104	Trace & Cover For Freeze Protection			All Items Subtotal (100 Series)	$4,028
201	Absorbers	16	Steel	12'Φx42' Bl to Bl 18' Packed section 2000 ft^3 - 3 1/2" Φ Pall Rings	
202	Fwd. Pumps	16	FRP	500 GPM, 40' HD, 10 HP	
203	Oxidizer Tower	1	Stl. & Epoxy	30'Φx24' HI w/foam Trough & Air Ring	
204	Air Diffusion Sys.	1	Steel	7500 SCFM, Blowers, Elec., Air Piping, Bldg.	
205	Sulfur Slurry Tk.	1	Steel & Epoxy	15000 Gal, 25 PSI	
206	Tank Agitator	1	Steel	Medium Ag., 15 HP.	
207	Slurry Pump	1	FRP.	100 GPM, 40 HD, 3 HP	
208	Rot. Vac. Filter Sys.	1	Stl.	Incls; Filter, Vac. Pump, Filtrate Receiver & Pump, Conveyor, Wash Tk, & Pump, Building	
209	Sulfur Melter	1	Steel	1200 Gal., 25 PSI, JKT. & Internal Coil, Insulate & Baffle	
210	Sulfur Fwd. Pump	1	Steel	10 GPM, 1 HP	
211	Sulfur Store Tk.	1	Steel	30,000 Gal. 1 WK API. S.G. = 2	
212	Agitator	1	Steel	Heavy, 5 HP	

FORM 39650 PRINTED IN U.S.A. R1-69

PRELIMINARY CAPITAL - DETAIL SHEET

SHEET 2 OF 6

PROJECT STRETFORD DIRECT PROCESS				JOB NUMBER 9212
PHASE PRE-1	CASE Case A	BY	DATE 1-31-80	EF NUMBER
SECTION NUMBER & NAME		SECTOR NUMBER & NAME		

FACTORS → BASE X ESC. X CAPACITY XQUANT. X [MATERIAL + CONDITION + COMPLEXITY] = MS(19)

ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION	
213	Drier Sys.	1	Steel	200 ft^2 W/Heating, Air or Vac. Sys., Feed & Disch. Conveyor, Bldg.	
214	Make-up Mix Tk.	1	Steel	2700 Gal, 8 Hr. Store	
215	Fwd. Pump	1	St.Stl.	100 GPM, 100' HD, 7 1/2 HP	
216	Lean Sol. Fd. Tk.	1	Steel Epoxy	36,000 Gal, 5 min. SG - 1.2	
217	Tower Cool Pumps	8	FRP	1000 GPM, 80' HD, 30 HP	
218	Purge Pump	1	FRP	100 GPM, 40' HD., 3 HP	
219	Mix Tk. Agitator	1	Steel	Medium, 25 HP	
220	Trace & Cover for Freeze Protection			All Items As Required	
				Subtotal (200 Series)	$5943
				Total (All Equipment)	$9971

PRELIMINARY CAPITAL - DETAIL SHEET

SHEET 3 OF 6

PROJECT STRETFORD DIRECT PROCESS				JOB NUMBER 9212
PHASE PRE-1	CASE Case A	BY	DATE 2-1-80	EF NUMBER
SECTION NUMBER & NAME		SECTOR NUMBER & NAME		

FACTORS → BASE X ESC. X CAPACITY X QUANT. X [MATERIAL + CONDITION + COMPLEXITY] = M$(19)

ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION	

Case A1 - Disposal of Purge Solution

Equipment as above (Sheets 1 and 2)	$ 9,971
Allowance (20%)	1,994
Total	11,965
Royalty (10% of capital)	1,197
Initial chemical charge	160
1980 Installed Capital Cost	$13,322

Case A2 - Recovery and Recycle of Purge Solution

Equipment as above (Sheets 1 and 2)	$ 9,971
Purge stream reductive incineration system (300 lb/hr salts)	1,150
Sub-total	11,121
Allowance (20%)	2,224
Total	$13,345
Royalty (10% of capital)	1,335
Initial chemical charge	160
1980 Installed Capital Cost	$14,840

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PRELIMINARY CAPITAL - DETAIL SHEET

PROJECT STRETFORD DIRECT PROCESS			JOB NUMBER 9212	SHEET 4 OF 6
PHASE PRE-1	CASE Case A1	BY	DATE	EF NUMBER
SECTION NUMBER & NAME		SECTOR NUMBER & NAME		

FACTORS	BASE X ESC. X CAPACITY	X QUANT. X	[MATERIAL +	CONDITION + COMPLEXITY]	= MS(19)
ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION	

Disposal of Purge Solution

1. Raw Materials:

Vanadate	$ 174,000/yr
ADA	887,000/yr
EDTA	24,000/yr
Sodium Carbonate	3,000/yr
Iron (Soluble)	Neg/yr
	$1,088,000/yr

2. By Products

Sulfur 12028 tons/yr x $90/ton = $1,083,000 (carbon)

3. Water Treatment or Disposal

"Sour" Water	132x10^6 gal/yr	No charge
"Purge" Water	9.28x10^6 lbs/yr	No charge
"Filter Wash"	5x10^6 gal/yr	No charge

4. Utilities

Electrical Power	10.1x10^6 KwH/yr	$303,000
150 Psig Steam	28x10^6 lb/yr	70,000
Process & Cooling Water	10,000 GPM	526,000
		$899,000

5. Manpower

14 men x 2000 hr/yr x $.15/MnHr	$420,000
1 supervisor 8760 hr x $20/MnHr	180,000
	$600,000

6. Maintenance, (5%), Capital Rec. (20%), Misc. (4%)

29% x capital $13,322,000	$3,864,000/yr

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PRELIMINARY CAPITAL - DETAIL SHEET

PROJECT STRETFORD DIRECT PROCESS				JOB NUMBER 9212
PHASE PRE-1	CASE Case Al	BY	DATE	EF NUMBER
SECTION NUMBER & NAME		SECTOR NUMBER & NAME		SHEET 5 OF 6

FACTORS	BASE X ESC. X CAPACITY	X QUANT. X	[MATERIAL +	CONDITION + COMPLEXITY]	= M$(19)
ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION	

Disposal of Purge Solution (Cont'd)

7.	Net Annualized Cost	$5,368,000/yr $0.294/ton of shale $0.494/bbl of oil
8.	Total Installed Capital	
	High, Dec. 1980	$17,320,000
	Probable, Dec. 1980	13,322,000
	Low, Dec. 1980	10,260,000

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PRELIMINARY CAPITAL - DETAIL SHEET

PROJECT STRETFORD DIRECT PROCESS				SHEET 6 OF 6
				JOB NUMBER 9212
PHASE PRE-1	CASE Case A2	BY	DATE	EF NUMBER
SECTION NUMBER & NAME		SECTOR NUMBER & NAME		

FACTORS →	BASE X ESC. X CAPACITY	X QUANT. X	[MATERIAL +	CONDITION + COMPLEXITY]	= M$(19)
ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION	

Recovery and Recycle of Purge Solution

1.	Raw Materials:		
	ADA		$887,000/yr
	EDTA		24,000/yr
			$911,000/yr
2.	By Products:		
	Sulfur, 12400 TPY		$1,116,000/yr (Credit)
3.	Water Treatment or Disposal		
	"Sour" Water	132×10^6 gal/yr	No charge
	"Filter Wash"	5×10^6 gal/yr	No charge
4.	Utilities:		
	Elec.	11.5×10^6 KwH/yr	$ 345,000/yr
	Stm.	42.9×10^6 lb/yr	107,000/yr
	Water	11000 Gpm	578,000/yr
	Gas	$15\ \overline{M}$ Btu/hr	328,000/yr
			$1,358,000/yr
5.	Manpower		
	18 men x 2000 hr/yr x $15/MnHr		$540,000/yr
	1 super. 8760 hr/yr x $20/MnHr		180,000/yr
			$720,000/yr
6.	Maint. (5%), Capital Rec. (20%), Misc. (4%)		$4,304,000/yr
7.	Net Annualized Cost		$6,177,000/yr $0.338/ton of shale $0.569/bbl of oil
8.	Total Installed Capital		
	High	Dec. 1980	$19,292,000
	Probable	Dec. 1980	14,840,000
	Low	Dec. 1980	11,426,000

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APPENDIX B

THREE-STAGE SELECTIVE ABSORPTION PLUS CLAUS SULFUR RECOVERY WITH SCOT TAIL GAS TREATMENT

PRELIMINARY CAPITAL - DETAIL SHEET

SHEET 1 OF 4

PROJECT 3 STAGE SELECTIVE ABSORPTION PLUS CLAUS SULFUR RECOVERY WITH SCOT TAIL GAS TREATMENT

JOB NUMBER 9212

PHASE	CASE	BY	DATE	EF NUMBER
PRE-1	Case B			

SECTION NUMBER & NAME

SECTOR NUMBER & NAME

FACTORS → BASE X ESC. X CAPACITY X QUANT. X [MATERIAL + CONDITION + COMPLEXITY] = M$(19)

ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION	
101	Gas Cooler	6	304 St.Stl.	12'Φx42' Bl-Bl, 10 PSI, 18' of Packing, 2000 ft^3	
102	Cooler Pump	6	304 St.Stl.	1000 GPM, 100' HD, 40 HP	
103	Exchangers	6	304 St.Stl.	5000 ft^2 U Tube, 14' Lg.	
104	Trace & Cover For Freeze Protection			All Items Subtotal (100 Series)	$4,028
201	1st. Stage Absorber	16	Steel	12'Φx42' Bl-Bl, 10 Trays	
202	Exchanger	16	Steel	829 ft^2	
203	Pump	16	D.I.	150 GPM, 100' HD, 7 1/2 HP	
204	Interchanger	16	Steel	287 ft^2	
205	1st Stage Desorber	3	Steel	12'Φ42' Bl-Bl, 10 Trays	
206	Condenser	3	Steel	3000 ft^2, Float, 14' Lg	
207	Pump	3	D.I.	716 GPM, 150' HD, 50 HP	
208	Pump	3	D.I.	639 GPM, 60' HD, 15 HP	
209	Reboiler	3	Steel	820 ft^2	
210	Compressor	3	Std.	6200 ACFM, 2 PSI, 25 HP	
211	Amine Recovery Reboil	1	Steel	2300 Gal., 154 ft^2	
212	Sludge Pump	1	D.I.	1/2 HP	
213	Sludge Accumulator	1	Steel	10 Day, 150 Gal	
214	Trace & Cover For Freeze Protection			All Items As Required Subtotal (200 Series)	$6,205
301	2nd Stg. Absorber	1	Steel	9'Φx36' Bl-Bl, 10 Trays	
302	Pump	1	D.I.	506 GPM, 150' HD, 25 HP	
303	Interchanger	1	Steel	700 ft^2	
304	Cooler	1	Steel	2200 ft^2	

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PRELIMINARY CAPITAL - DETAIL SHEET

SHEET 2 OF 4

PROJECT 3 STAGE SELECTIVE ABSORPTION PLUS CLAUS SULFUR RECOVERY WITH SCOT TAIL GAS TREATMENT			JOB NUMBER 9212
PHASE	CASE Case B	BY	DATE
EF NUMBER			
SECTION NUMBER & NAME		SECTOR NUMBER & NAME	

FACTORS	BASE X ESC. X CAPACITY	X QUANT. X	[MATERIAL +	CONDITION + COMPLEXITY]	= M$(19)
ITEM	**NAME OF FACILITY**	**QUANT.**	**CONSTRUCTION MATERIAL**	**DESCRIPTION**	
305	2nd Stg. Desorber	1	Steel	9'Φx36' Bl-Bl, 10 Trays	
306	Pump	1	D.I.	432 GPM, 150' HD, 40 HP	
307	Pump	1	D.I.	432 GPM, 150' HD, 40 HP	
308	Reboiler	1	Steel	900 ft^2	
309	Condenser	1	Steel	2000 ft^2	
310	Compressor	1	Std.	6200 ACFM, 2 PSI, 25 HP	
311	Trace & Cover For Freeze Protection			All Items As Required	
				Subtotal (300 Series)	$957
401	3rd Stg. Absorber	1	Steel	6'Φx30' Bl-Bl, 10 Trays	
402	Pump	1	D.I.	200 GPM, 100', 20 HP	
403	Interchanger	1	Steel	187 ft^2	
404	Cooler	1	Steel	823 ft^2	
405	3rd Stg. Desorber	1	Steel	6'Φx30' Bl-Bl, 10 Trays	
406	Pump	1	D.I.	160 GPM, 150' HD, 15 HP	
407	Pump	1	D.I.	160 GPM, 150' HD, 15 HP	
408	Reboiler	1	Steel	300 ft^2	
409	Condenser	1	Steel	731 ft^2	
410	Compressor	1	Steel	2123 CFM, 7 1/2 HP	
411	Trace & Cover For Freeze Protection			All Items As Required	
				Subtotal (Series 400)	$462
500	3 Stage Claus Unit Trace & Cover As Required	Sys.		2123 scfm, 27.4 mole % H_2S 35.8 TPD of Sulfur	$566

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PRELIMINARY CAPITAL - DETAIL SHEET

SHEET 3 OF 4

PROJECT 3 STAGE SELECTIVE ABSORPTION PLUS CLAUS SULFUR RECOVERY WITH SCOT TAIL GAS TREATMENT

JOB NUMBER 9212

PHASE PRE-1

CASE Case B

BY

DATE

EF NUMBER

SECTION NUMBER & NAME

SECTOR NUMBER & NAME

FACTORS → BASE X ESC. X CAPACITY X QUANT. X [MATERIAL + CONDITION + COMPLEXITY] = M$(19)

ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION	
500	SCOT tail Gas Treatment System Trace & Cover As Required	Sys.		3225 scfm, 0.035 mole % H_2S 164 bb/day of sulfur	$ 358
				Total (All Equipment)	$12,576
	Allowance (20%)				$ 2,515
	Royalty (Per Dow Chemical USA)				300
	Initial Chemical Charge				160
		1980 Installed Capital Cost			$15,551

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PRELIMINARY CAPITAL - DETAIL SHEET

SHEET 4 OF 4

PROJECT 3 STAGE SELECTIVE ABSORPTION PLUS CLAUS SULFUR RECOVERY WITH SCOT TAIL GAS TREATMENT

JOB NUMBER 9212

PHASE

CASE Case B

BY

DATE

EF NUMBER

SECTION NUMBER & NAME

SECTOR NUMBER & NAME

FACTORS → BASE X ESC. X CAPACITY X QUANT. X [MATERIAL + CONDITION + COMPLEXITY] = M$(19)

ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION
1.	Raw Materials:			
	MDEA	13.14 tons/yr		$ 24,000/yr
2.	By Products:			
	Sulfur	13,016 Tons/yr		$1,171,000/yr (Credit)
3.	To Water Treatment or Disposal:			
	"Sour" Water	133.4x10^{6} gal/yr		No charge
	"Sludge" Water	3x10^{4} lb/yr		No charge
4.	Utilities:			
	Elec. Power	5.3x10^{6} KwH/yr		$ 158,000/yr
	Steam, Net	2873x10^{6} lb/yr		7,183,000/yr
	Cool Water	1.5x10^{10} gal/yr		1,545,000/yr
				$8,886,000/yr
5.	Manpower:			
	10 Operators			$300,000/yr
	1 Supervisor			180,000/yr
				$480,000/yr
6.	Maintenance (5%), Capital Rec. (20%), Misc. (4%)			
	20% x Capital $15,551,000			$4,510,000/yr
7.	Net Annualized Cost			$12,729,000/yr $0.069/Ton of Shale $1.172/bbl of Oil
8.	Total Installed Capital			
	High, Dec. 1980			$20,216,000
	Prob., Dec. 1980			15,551,000
	Low, Dec. 1980			11,974,000

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APPENDIX C

ONE-STAGE SELECTIVE ABSORPTION PLUS INDIRECT STRETFORD SULFUR RECOVERY

PRELIMINARY CAPITAL - DETAIL SHEET

SHEET 1 OF 3			
PROJECT I STAGE SELECTIVE ABSORPTION PLUS INDIRECT STRETFORD SULFUR RECOVERY			JOB NUMBER 9212
PHASE PRE-1	CASE C	BY	DATE 2-4-80
EF NUMBER			
SECTION NUMBER & NAME	SECTOR NUMBER & NAME		

FACTORS →	BASE X ESC. X CAPACITY	X QUANT. X	[MATERIAL +	CONDITION + COMPLEXITY]	= M$(19)
ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION	
101	Gas Coolers	6	304 St.Stl.	12'Φx42' Bl-Bl, 10 PSI, 18' Pack Sec. 2000 ft^3 3 1/2" Pall Rings	
102	Cooler Pumps	6	304 St.Stl.	1000 GPM, 100' HD, 40 HP	
103	Exchangers	6	304 St.Stl.	5000 ft^2, U Tube, 14' LG	
104	Trace & Cover For Freeze Protection			All Items Subtotal (100 Series)	$4,028
201	Selective Absorber	16	Steel	12'Φx42' Bl to Bl 10 Valve Trays	
202	Exchanger	16	Steel	57/ft^2	
203	Pump	16	D.l.	150 GPM, 100' HD, 7 1/2 HP	
204	Interchanger	16	Steel	287 ft^2	
205	Strip Column	3	Steel	12'Φx42' Bl-Bl 10 Plate	
206	Condenser	3	Steel	3000 ft^2, Float, 14' LG	
207	Column Pump	3	D.l.	716 GPM, 150' HD, 50 HP	
208	Reboil Pump	3	D.l.	639 GPM, 50' HD, 15 HP	
209	Strip Col. Reboiler	3	Steel	722 ft^2	
210	Compressor	3	Std.	6200 ACFM, 2 PSI	
211	Amine Recv. Reboil	1	Steel	2300 Gal., 154 ft^2	
212	Sludge Pump	1	D.l.	1/2 HP	
213	Sludge Accumulator	1	Steel	10 Day, 150 gal.	
214	Trace & Cover For Freeze Protection			All Items As Required Subtotal (200 Series)	$5,957
301	H$_2$S Absorber	1	Steel	10'x28' Bl-Bl, 13' Pack, Sec. 2200 ft^3-3 1/2" Pall Rings	
302	Oxidizer Tower	1	Steel Epoxy	30'Φx24' W/Foam Trough Air Ring	

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PRELIMINARY CAPITAL - DETAIL SHEET

SHEET 2 OF 3

PROJECT: I STAGE SELECTIVE ABSORPTION PLUS INDIRECT STRETFORD SULFUR RECOVERY

JOB NUMBER: 9212

PHASE: PRE-1

CASE: C

BY:

DATE: 2-4-80

EF NUMBER:

SECTION NUMBER & NAME:

SECTOR NUMBER & NAME:

FACTORS → BASE X ESC. X CAPACITY X QUANT. X [MATERIAL + CONDITION + COMPLEXITY] = M$(19)

ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION	
303	Air Diffusion System	1	Steel	7500 SCFM, Blowers, Elec. Air Pipe, Bldg.	
304	Sulfur Slurry Tk.	1	Steel Epoxy	15000 Gal. 25 psi	
305	Tank Agitator	1	Steel	Med., 15 HP	
306	Slurry Pump	1	FRP	100 GPM, 40' HD, 3 HP	
307	Rot. Vac. Filter	1	Std.	Filter, Vac Pump, Filtrate Receiver & Pump, Conveyor, Wash Tk. & Pump, Bldg.	
308	Sulfur Melter	1	Steel	1200 Gal., 25 Psi, JKT. & Internal Coil, Insulate & Baffle	
309	Sulfur Fwd. Pump	1	Steel	10 GPM, 1 HP, T&C	
310	Sulfur Store Tk.	1	Steel	30,000 Gal. T&C, 1 wk API s.g. = 2	
311	Agitator	1	Steel	Heavy, 5 HP	
312	Drier Sys	1	Steel	200 ft^2 w/Heating, Air or Vac. Sys., Feed & Disch. Conveyor, Bldg.	
313	Make-up Mix. Tk.	1	Steel	27,000 Gal., 8 Hr Store	
314	Fwd. Pump	1	St.Stl.	100 GPM, 100' HD, 7 1/2 HP	
315	Lean Sol. Fd. Tk.	1	Steel Epoxy	36,000 Gal. 5 min., s.g.=1.2	
316	Purge Pump	1	FRP	100 GPM, 40; HD., 3 HP	
317	Mix Tk. Agitator	1	Steel	Medium, 25 HP	
318	Trace & Cover For Freeze Protection			All Items As Required	
				Subtotal (300 Series)	$ 2,924
				Total (All Equipment)	$12,909

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PRELIMINARY CAPITAL - DETAIL SHEET

SHEET 3 OF 3				
PROJECT I STAGE SELECTIVE ABSORPTION PLUS INDIRECT STRETFORD SULFUR RECOVERY				JOB NUMBER 9212
PHASE PRE-1	CASE C	BY	DATE 2-4-80	EF NUMBER
SECTION NUMBER & NAME		SECTOR NUMBER & NAME		

FACTORS	BASE X ESC. X CAPACITY	X QUANT. X	[MATERIAL +	CONDITION + COMPLEXITY]	= M$(19)
ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION	

Case B1 - Disposal of Stretford Purge Solution

Equipment as above (sheets 1-3)	$12,909
Allowance (20%)	2,582
Total	$15,491
Royalty (10% of capital)	1,549
Initial Chemical Charge	160
1980 Installed Capital Cost	$17,200

Case B2 - Recovery and Recycle of Stretford Purge Solution

Equipment as above (sheets 1-3)	$12,909
Stretford Purge Stream Reductive Incineration System	1,150
Subtotal	$14,059
Allowance (20%)	2,812
Total	$16,871
Royalty (10% of capital)	1,687
Initial Chemical Charge	160
1980 Installed Capital Cost	$18,718

PRELIMINARY CAPITAL - DETAIL SHEET

SHEET 1 OF 4

PROJECT
I STAGE SELECTIVE ABSORPTION PLUS INDIRECT STRETFORD SULFUR RECOVERY

JOB NUMBER 9212

PHASE	CASE	BY	DATE	EF NUMBER
	C1			

SECTION NUMBER & NAME	SECTOR NUMBER & NAME

FACTORS → BASE X ESC. X CAPACITY X QUANT. X [MATERIAL + CONDITION + COMPLEXITY] = M$(19)

ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION

Disposal of Purge Solution

1. Raw Materials:

Methyl Diethanolamine	$ 28,000/yr
ADA	954,000/yr
EDTA	24,000/yr
Vanadate	181,000/yr
Sodium Carbonate	Neg/yr
Iron	3,000/yr
	$1,190,000/yr

2. By Products

Sulfur	12,516 ton/yr	$1,130,000/yr (Credit)

3. To Water Treatment or Disposal:

"Sour" Water	$132x10^6$ gm/yr	No charge
"Purge" Water	$9.65x10^6$ lb/yr	No charge
"Sludge" Water	$3x10^4$ lb/yr	No charge
"Filter Wash"	$5x10^6$ gal/yr	No charge

4. Utilities:

Electrical Power	$7.8x10^6$ KwH/yr	$ 234,000/yr
150 Psig Steam	$1525x10^6$ kb/yr	3,812,000/yr
Water	24M GPM	1,261,000/yr
		$5,307,000/yr

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PRELIMINARY CAPITAL - DETAIL SHEET

SHEET 2 OF 4

PROJECT: I STAGE SELECTIVE ABSORPTION PLUS INDIRECT STRETFORD DESULFURIZATION

JOB NUMBER: 9212

PHASE:

CASE: C1

BY:

DATE:

EF NUMBER:

SECTION NUMBER & NAME:

SECTOR NUMBER & NAME:

FACTORS ▶ BASE X ESC. X CAPACITY X QUANT. X [MATERIAL + CONDITION + COMPLEXITY] = M$(19)

ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION	
5.	Manpower				
	15 men x 2000 hr/yr x $15/yr			$450,000/yr	
	1 supervisor			180,000/yr	
				$630,000/yr	
6.	Maintenance (5%), Capital Rec. (20%), Misc. (4%)				
	29% x $17,200,000			$4,988,000/yr	
7.	Net Annualized Cost			$10,985,000/yr $0.602/ton of shale $1.011/bbl of oil	
8.	Total Installed Capital				
	High, Dec. 1980			$22,360,000	
	Probable, Dec. 1980			17,200,000	
	Low, Dec. 1980			13,244,000	

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PRELIMINARY CAPITAL - DETAIL SHEET

SHEET 3 OF 4

PROJECT: I STAGE SELECTIVE ABSORPTION PLUS INDIRECT STRETFORD DESULFURIZATION

JOB NUMBER: 9212

PHASE:

CASE: C2

BY:

DATE:

EF NUMBER:

SECTION NUMBER & NAME:

SECTOR NUMBER & NAME:

FACTORS: BASE X ESC. X CAPACITY X QUANT. X [MATERIAL + CONDITION + COMPLEXITY] = M$(19)

ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION

1.	Raw Materials:		
	Methyl Diethanolamine		$ 28,000/yr
	ADA		954,000/yr
	EDTA		24,000/yr
			$1,006,000/yr
2.	By Products		
	Sulfur	12,903 TPY x $90/T	$1,160,000/yr (Credit)
3.	Watertreat or Disposal		
	"Sour" Water	$133.4x10^6$ gal/yr	No charge
	"Sludge" Water	$3x10^4$ lb/yr	No charge
	"Filter Wash"	$5x10^6$ gal/yr	No charge
4.	Utilities:		
	Elec. Power	$9.2x10^6$ KwH/yr	$ 276,000/yr
	Steam	$1540x10^6$ lb/yr	3,850,000/yr
	Water	25M GPM	1,314,000/yr
	Gas	15M Btu/hr	328,000/yr
			$5,768,000/yr
5.	Manpower		
	19 men x 2000 hr/yr x $15/hr		$570,000/yr
	1 supervisor		180,000/yr
			$750,000/yr
6.	Maintenance (5%), Capital Rec. (20%), Misc. (4%)		
	29% x $18,718,000		$5,428,000/yr

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PRELIMINARY CAPITAL - DETAIL SHEET

SHEET	4 OF 4
PROJECT	I STAGE SELECTIVE ABSORPTION PLUS INDIRECT STRETFORD DESULFURIZATION
JOB NUMBER	9212
PHASE	
CASE	C2
BY	
DATE	
EF NUMBER	
SECTION NUMBER & NAME	
SECTOR NUMBER & NAME	

FACTORS ➔ BASE X ESC. X CAPACITY X QUANT. X [MATERIAL + CONDITION + COMPLEXITY] = M$(19)

ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION	
7.	Net Annualized Cost			$11,792,000/yr $0.646/ton of shale $1.086/bbl of oil	
8.	Total Installed Capital:				
	High, Dec. 1980			$24,333,000	
	Probable, Dec. 1980			$18,718,000	
	Low, Dec. 1980			$14,413,000	

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APPENDIX D

DIAMOX PROCESS PLUS CLAUS SULFUR RECOVERY WITH BSRP TAIL GAS TREATMENT

PRELIMINARY CAPITAL - DETAIL SHEET

SHEET 1 OF 3

PROJECT: DIAMOX PROCESS PLUS CLAUS SULFUR RECOVERY WITH BSRP TAIL GAS TREATMENT

JOB NUMBER: 9212

PHASE:

CASE: Case D

BY:

DATE:

EF NUMBER:

SECTION NUMBER & NAME:

SECTOR NUMBER & NAME:

FACTORS → BASE X ESC. X CAPACITY X QUANT. X [MATERIAL + CONDITION + COMPLEXITY] = M$(19)

ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION	= M$(19)
101	Gas Coolers	6	304 St.Stl.	12'Φx42' Bl to Bl, 10 psi 18' packed section, 2000 ft^3-3 1/2"Φ Pall Rings	
102	Cooler Circ. Pumps	6	304 St.Stl.	1000 gpm, 100" Hd, 40 HP	
103	Exchangers	6	304 St.Stl.	5000 ft^2, U Tube, 14' LG Tubes	
104	Trace & Cover For Freeze Protection			All Items	$4,028
204	Absorbers	6	Steel	12'Φx72' High w/10' skirt, 6 sets spray nozzles deliver 3,000 gpm; 6 sets bulkheads and overflow wiers for liquor collection and visors for gas flow.	
202	Absorber Pumps	30	D.I.	3000 gpm pumps to deliver liquor to spray nozzles at 40 psig pressure	
203	Stripper Feed Pumps	6	D.I.	3000 gpm pumps to deliver liquor to strippers at 30 psig pressure	
204	Stripper Bottoms Pumps	4	D.I.	4500 gpm pumps @ 30 psig pressure	
205	Acid Gas Strippers	4	Steel	12'Φx7 trays @ 24" spacing	
206	Heat Interchanger	4	Steel	18,000 sq.ft. multipass, cross flow	
207	Cooling Water Exchanger	4	Steel	18,000 sq.ft. multipass, cross flow	
208	Refrig. Exchanger	4	Steel	2200 sq. ft., 40°F chilled water	
209	Absorber Liquor Purge Pump	4	CI	180 gpm @ 30 ft. head	
210	Absorber Liquor Storage	1	Steel	540,000 gal., 48'Φx40'h	

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PRELIMINARY CAPITAL - DETAIL SHEET

SHEET 2 OF 3

PROJECT: DIAMOX PROCESS PLUS CLAUS SULFUR RECOVERY WITH BSRP TAIL GAS TREATMENT

JOB NUMBER: 9212

PHASE:

CASE: Case D

BY:

DATE:

EF NUMBER:

SECTION NUMBER & NAME:

SECTOR NUMBER & NAME:

FACTORS → BASE X ESC. X CAPACITY X QUANT. X [MATERIAL + CONDITION + COMPLEXITY] = M$(19)

ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION	
211	Absorber Feed Pump	6	CI	3000 gpm pumps @ 60 psig head	
212	Chilled Water Refrig. System	1	Std.	1250 Tons, $0^{\circ}C$	
213	Trace & Cover for Freeze Protection			All Items As Required	
				Subtotal (200 Series)	$19,769
300	3 Stage Claus Unit Trace & Cover as Required	Sys.		10,045 scfm, 6 mole % H_2S 35.2 TPD of Sulfur	$ 1,647
400	BSPR Tail Gas Treatment Unit Trace & Cover as Required	Sys.		11,137 scfm, 0.031 mole % H_2S 427 lb/day	$ 1,021
				Total (Equipment)	$26,465
	Allowance		(20%)		5,293
				Total	$31,758
	Royalty	(Per R. M. Parsons Co.)			900
	Initial Chemical Charge (BSPR Unit)				83
		1980 Installed Capital Cost			$32,741

FORM 39650 PRINTED IN U.S.A. R1-69

PRELIMINARY CAPITAL - DETAIL SHEET

SHEET 3 OF 3

PROJECT: DIAMOX ABSORPTION PLUS CLAUS SULFUR RECOVERY WITH BSRP TAIL GAS TREATMENT

JOB NUMBER: 9212

PHASE:

CASE: Case D

BY:

DATE:

EF NUMBER:

SECTION NUMBER & NAME:

SECTOR NUMBER & NAME:

FACTORS → BASE X ESC. X CAPACITY X QUANT. X [MATERIAL + CONDITION + COMPLEXITY] = M$(19)

ITEM	NAME OF FACILITY	QUANT.	CONSTRUCTION MATERIAL	DESCRIPTION
1.	Raw Materials: (Parsons' Info)			
	Catalysts, Chemicals, Initial Charge			\$82,680
	Consumption \$230/day x 365			\$84,000/yr
2.	By Products			
	Sulfur 12830 TPY			\$1,150,000/yr (Credit)
3.	Water Treatment or Disposal:			
	148×10^6 gal/yr			No charge
4.	Utilities:			
	Electric Power 53.9×10^6 KwH/yr			\$ 1,618,000/yr
	Steam, Net 4480×10^6 lb/yr			\$11,530,000/yr
	Cool H_2O 1.95×10^{10} gal/yr			\$ 1,950,000/yr
				\$15,098,000/yr
5.	Manpower:			
	10 Operators			\$300,000/yr
	1 Supervisor			180,000/yr
				\$480,000/yr
6.	Maintenance (5%), Capital Rec. (20%), Misc. (4%)			
	29% x capital \$32,741,000			\$9,945,000
7.	Net Annualized Cost			\$24,007,000/yr \$1.315/ton of shale \$2.210/bbl of oil
8.	Total Installed Capital			
	High, Dec. 1980			\$42,563,000
	Prob., Dec. 1980			\$32,741,000
	Low, Dec. 1980			\$25,211,000

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END